Degradation Mechanisms of Electrochemically Cycled Graphite Anodes in Lithium-ion Cells

Sandeep Bhattacharya

University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation

https://scholar.uwindsor.ca/etd/5090
DEGRADATION MECHANISMS OF ELECTROCHEMICALLY CYCLED GRAPHITE ANODES IN LITHIUM-ION CELLS

By

Sandeep Bhattacharya

A Dissertation
Submitted to the Faculty of Graduate Studies through the Department of Mechanical, Automotive & Materials Engineering in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario, Canada

2014

© 2014 Sandeep Bhattacharya
Degradation Mechanisms of Electrochemically Cycled Graphite Anodes in Lithium-ion Cells

By

Sandeep Bhattacharya

APPROVED BY:

________________________________________________________________________
A. Sun (External Examiner)
Mechanical and Materials Engineering, University of Western Ontario

________________________________________________________________________
S. H. Eichhorn
Chemistry & Biochemistry

________________________________________________________________________
D. O. Northwood
Mechanical, Automotive and Materials Engineering

________________________________________________________________________
A. Edrisy
Mechanical, Automotive and Materials Engineering

________________________________________________________________________
A. R. Riahi (Co-Advisor)
Mechanical, Automotive and Materials Engineering

________________________________________________________________________
A. T. Alpas (Advisor)
Mechanical, Automotive and Materials Engineering

May 20, 2014
DECLARATION OF
CO-AUTHORSHIP/PREVIOUS PUBLICATIONS

I. Co-Authorship Declaration

I hereby declare that this dissertation incorporates research results obtained by the author under the co-supervision of Dr.Ahmet T. Alpas and Dr.A. Reza Riahi. The experiments involving electrodeposition of tin on carbon fibres described in Chapter 7 were performed by Dr.Mehdi Shafiei (Novelis Global Research and formerly of University of Windsor). The interpretation of electron images using scanning and transmission electron microscopes was performed jointly by Dr.Shafiei and the author himself.

I certify that, with the above qualification, this dissertation, and the research to which it refers, is the product of my own work.

II. Declaration of Previous Publications

This dissertation includes five original papers that have been previously published or submitted in peer-reviewed journals, and one more to be submitted for publication, as follows:

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Publication details</th>
<th>Publication status</th>
</tr>
</thead>
</table>

4  S. Bhattacharya, A.T. Alpas, Micromechanisms of solid electrolyte interphase formation on electrochemically cycled graphite electrodes in lithium-ion cells, Carbon, 50 (2012) 5359-5371.


I certify that I have obtained a written permission from the copyright owner(s) to include the above published material(s) in my dissertation. I certify that the above material describes work completed during my registration as graduate student at the University of Windsor.

I declare that, to the best of my knowledge, my dissertation does not infringe upon anyone’s copyright nor violate any proprietary rights and that any ideas, techniques, quotations, or any other material from the work of other people included in my dissertation, published or otherwise, are fully acknowledged in accordance with the standard referencing practices. Furthermore, to the extent that I have included copyrighted material that surpasses the bounds of fair dealing within the meaning of the Canada Copyright Act, I certify that I have obtained a written permission from the copyright owner(s) to include such material(s) in my dissertation.
I declare that this is a true copy of my dissertation, including any final revisions, as approved by my dissertation committee and the Graduate Studies office, and that this dissertation has not been submitted for a higher degree to any other University or Institution.
ABSTRACT

This research is aimed at developing advanced characterization methods for studying the surface and subsurface damage in Li-ion battery anodes made of polycrystalline graphite and identifying the degradation mechanisms that cause loss of electrochemical capacity. Understanding microstructural aspects of the graphite electrode degradation mechanisms during charging and discharging of Li-ion batteries is of key importance in order to design durable anodes with high capacity.

An in-situ system was constructed using an electrochemical cell with an observation window, a large depth-of-field digital microscope and a micro-Raman spectrometer. It was revealed that electrode damage by removal of the surface graphite fragments of 5-10 μm size is the most intense during the first cycle that led to a drastic capacity drop. Once a solid electrolyte interphase (SEI) layer covered the electrode surface, the rate of graphite particle loss decreased. Yet, a gradual loss of capacity continued by the formation of interlayer cracks adjacent to SEI/graphite interfaces. Deposition of co-intercalation compounds, LiC₆, Li₂CO₃ and Li₂O, near the crack tips caused partial closure of propagating graphite cracks during cycling and reduced the crack growth rate. Bridging of crack faces by delaminated graphite layers also retarded crack propagation.

The microstructure of the SEI layer, formed by electrochemical reduction of the ethylene carbonate based electrolyte, consisted of ~5-20 nm sized crystalline domains (containing Li₂CO₃, Li₂O₂ and nano-sized graphite fragments) dispersed in an amorphous matrix. During the SEI formation, two regimes of Li-ion diffusion were identified at the electrode/electrolyte interface depending on the applied voltage scan rate (dV/dt). A low Li-
ion diffusion coefficient ($D_{Li^+}$) at $dV/dt < 0.05 \text{ mVs}^{-1}$ produced a tubular SEI that uniformly covered the graphite surface and prevented damage at 25°C. At 60°C, a high $D_{Li^+}$ formed a Li$_2$CO$_3$-enriched SEI and ensued a 28% increase in the battery capacity at 25°C.

On correlating the microscopic information to the electrochemical performance, novel Li$_2$CO$_3$-coated electrodes were fabricated that were durable. The SEI formed on pre-treated electrodes reduced the strain in the graphite lattice from 0.4% (for uncoated electrodes) to 0.1%, facilitated Li-ion diffusion and hence improved the capacity retention of Li-ion batteries during long-term cycling.
DEDICATION

This dissertation is dedicated to

my late grandfather, Atul C. Mukherjee,

my parents, Kishore and Anuroma Bhattacharya,

my sisters, Sanjukta and Sudeshna,

my brother-in-law, Sougat Ray,

and

to my wife,

Debjani.

Thank you for believing in me.
ACKNOWLEDGEMENTS

First and foremost, I offer my sincerest gratitude and appreciation to Dr. Ahmet T. Alpas for providing continuous motivation and encouragement especially in the most challenging times of this long journey. I am grateful to Dr. Reza Riahi for his valuable help and suggestions that helped me immensely in this research.

Sincere thanks to my committee members, Dr. Derek Northwood, Dr. Afsaneh Edrisy, Dr. S. Holger Eichhorn for their helpful suggestions. Valuable and insightful discussions with Dr. Yue Qi and Dr. Stephen J. Harris of the General Motors Global R&D Centre have helped to improve the quality of the research work. Dr. X. Meng-Burany's contribution to discussions on TEM analyses is greatly appreciated. I would like to thank Dr. Gianluigi Botton and Dr. Glynis de Silveira for providing access to the Canadian Center of Electron Microscopy (CCEM) at McMaster University, Hamilton, Canada, and to Ms. Sharon Lackie for her help in operating the environmental SEM located in the Great Lakes Institute for Environmental Research. Technical help from Mr. Andrew Jenner and Mr. Steve Budinsky is greatly acknowledged.

I am thankful to the faculty and the staff at the Department of Mechanical, Automotive and Materials Engineering including all past and current researchers of the Tribology of Materials Research Centre for their help and assistance.

Sincere thanks to the Natural Sciences and Engineering Research Council of Canada (NSERC) for providing financial support.
## TABLE OF CONTENTS

DEENTICATION OF CO-AUTHORSHIP/PREVIOUS PUBLICATIONS .......... iii  

ABSTRACT ................................................................................................................ vi  

DEDICATION ........................................................................................................ viii  

ACKNOWLEDGEMENTS .................................................................................... ix  

LIST OF TABLES ................................................................................................ xvii  

LIST OF FIGURES ................................................................................................ xviii  

LIST OF ABBREVIATIONS/SYMBOLS ............................................................ xxxiii  

CHAPTER 1: Research Background ................................................................. 1  

1.1. Introduction ................................................................................................. 1  

1.2. Working Principle of a Lithium-ion Battery .............................................. 6  

1.3. Structure of Graphite ................................................................................ 8  

1.4. Lithium Intercalation in Graphite .............................................................. 12  

1.5. Electrochemical Behavior of Graphitic Carbons with Lithium ............... 16  

1.6. Mechanisms of SEI Formation ................................................................. 20  

1.7. Electrochemical Cycling-induced Surface Changes of Graphite Electrodes ........ 24  

1.8. In-situ Observations of Graphite Damage and SEI Morphology ............ 30
3.2.3. Preparation of Cross-sectional TEM Samples using FIB in situ Lift-out Technique

3.3. Results and Discussions

3.3.1. Observation of Subsurface Damage in Cycled Graphite Electrodes

3.3.2. Characterization of Subsurface Cracks in Graphite

3.3.3. Mechanisms of Crack Formation and Propagation during Lithiation/De-lithiation

3.4. Conclusions

Bibliography

CHAPTER 4: Micromechanisms of Solid Electrolyte Interphase Formation on Electrochemically Cycled Graphite Electrodes in Lithium-ion Cells

4.1. Introduction

4.2. Experimental

4.2.1. Description of material and electrochemical tests

4.2.2. Solid electrolyte interphase characterization techniques

4.3. Results

4.3.1. Linear sweep voltammetry at different scan rates

4.3.2. Description of solid electrolyte interphase formed on graphite surface at different scan rates

4.3.3. Morphology and microstructure of solid electrolyte interphase

4.4. Discussion
4.4.1. Effect of Li\(^+\) diffusion kinetics on solid electrolyte interphase formation .......... 117
4.4.2. Micromechanisms of solid electrolyte interphase formation ............................... 120
4.5. Conclusions .................................................................................................................. 122

Bibliography ......................................................................................................................... 123

CHAPTER 5: Thermal Cycling Induced Capacity Enhancement of Graphite Anodes in Lithium-ion Cells ............................................................................................................... 129

5.1. Introduction ..................................................................................................................... 129
5.2. Experimental .................................................................................................................. 132
5.2.1. Description of Materials and Voltammetry Tests .................................................... 132
5.2.2. Microscopic and Spectroscopic Techniques ............................................................. 133
5.3. Results ........................................................................................................................... 135
5.3.1. Planar Capacity at Different Temperatures ............................................................... 135
5.3.2. Description of Graphite Electrode Surface Damage and SEI Formation ............... 136
5.3.3. Morphology of Graphite Surfaces with SEI ............................................................ 141
5.3.4. Transmission Electron Microscopy of the SEI formed at 60\(^\circ\)C ............................ 144
5.3.5. Compositional Analyses of SEI .............................................................................. 146
5.4. Discussion ...................................................................................................................... 150
5.4.1. Variations in Li-ion Diffusion Kinetics with Temperature ..................................... 150
5.4.2. Improvement of Capacity by Pre-Cycling at 60\(^\circ\)C ............................................. 157
5.5. Conclusions .................................................................................................................... 159
CHAPTER 6: Electrochemical Cycling Behaviour of Li$_2$CO$_3$ Pre-treated Graphite Anodes: SEI Formation and Graphite Damage Mechanisms

6.1. Introduction

6.2. Experimental

6.2.1. Description of Electrodes and Li$_2$CO$_3$ Deposition Process

6.2.2. Cell Assembly and Voltammetry Tests

6.2.3. Experimental Setup for \textit{in situ} Optical Microscopy and micro-Raman Spectroscopy

6.2.4. XPS and FTIR Analyses of Pre-treated Electrodes

6.2.5. Transmission Electron Microscopy (TEM) of SEI

6.3. Results

6.3.1. \textit{In situ} Observations of Changes in Morphological Features of Electrode Surface using Optical Microscopy

6.3.2. \textit{In situ} Strain Measurement on Graphite Surface using Raman Spectroscopy

6.3.3. Electrochemical Capacity of Electrodes during Prolonged Cycling

6.3.4. Characterization of SEI using XPS and FTIR

6.3.5. High Resolution TEM Analyses of SEI

6.4. Discussion: Role of the Pre-treatment on Improving Cyclic Performance

6.5. Conclusions

Bibliography

xv
CHAPTER 7: Capacity Fading Mechanisms of a Sn-Carbon Fibre Composite Anode
Cycled in Lithium-ion Cells ................................................................. 201

7.1. Introduction .................................................................................. 201

7.2. Experimental ................................................................................ 204

7.2.1. Description of Materials Used .................................................. 204

7.2.2. Description of Galvanostatic Tests ............................................. 205

7.2.3. SEM and TEM Investigations of Coated and Uncoated CFP ......... 207

7.2.4. In-situ Optical and Raman Spectroscopy during Cyclic Voltammetry
Experiments ...................................................................................... 208

7.3. Results .......................................................................................... 209

7.3.1. Capacity of Coated and Uncoated CFP ....................................... 209

7.3.2. SEM Observations of Cycled Uncoated-CFP and Sn-CFP ............ 210

7.3.3. TEM Characterization of Electrochemically Cycled Sn-CFP .......... 212

7.4. Discussion .................................................................................... 214

7.4.1. Surface Changes in Sn-CFP Observed in the Time Scale of Electrochemical
Tests .................................................................................................. 214

7.4.2. Li-Ion Diffusion in Coated and Uncoated Fibres ......................... 218

7.4.3. Mechanisms of Capacity Retention in Coated and Uncoated Fibres .... 219

7.5. Conclusions ................................................................................ 222

Bibliography ....................................................................................... 223

CHAPTER 8: Summary and Conclusions ............................................. 230
8.1. Summary of Main Results .................................................................................................... 230

8.1.1. Instantaneous Damage in Graphite Electrodes ........................................................ 230

8.1.2. Damage Accumulation during Progressive Cycling ................................................. 231

8.1.3. Micromechanisms of SEI Formation ......................................................................... 231

8.1.4. Capacity Enhancement by Pre-treatment at 60°C .................................................... 232

8.1.5. Improvement of Electrochemical Cycling Behaviour of Graphite Anodes by 

Li₂CO₃ Pre-treatment .............................................................................................................. 232

8.1.6. Sn-Carbon Fibre Composite Anodes for Li-ion Batteries .................................... 233

8.2. General Conclusions ............................................................................................................ 234

8.2.1. Electrode Damage Map (EDM) and its Applications .............................................. 234

8.2.1. Scientific and Technological Impact ........................................................................... 235

8.3. Future Work .......................................................................................................................... 236

8.3.1. Fracture Mechanics Analyses of Crack Growth ....................................................... 236

8.3.2. Electrochemical Properties of Mesocarbon Microbeads (MCMB) ....................... 237

8.3.3. Damage Mechanisms of Si particles in Al-Si Electrodes .................................... 239

Bibliography .................................................................................................................................. 246

APPENDIX: Copyright Releases from Publications ................................................ 247

VITA AUCTORIS ...................................................................................................... 283
LIST OF TABLES

Table 1.1. Characteristics of commonly used rechargeable batteries......................................................2

Table 1.2. SEI thickness values as reported in the literature........................................................................30

Table 4.1. Peak current density ($i_p/A$) and voltage ($v_p$) values observed during linear sweep voltammetry tests performed from $V = 3.00$ V → 0.02 V at $dV/dt = 0.05$-5.00 mVs$^{-1}$.................................................................................................................................107

Table 5.1. Peak comparative elemental composition analyses using XPS of graphite electrode surfaces in Fig.5.11.................................................................................................................................147

Table 5.2. Summary of compositional and microstructural analyses of the SEI formed at 25 and 60°C........................................................................................................................................149

Table 5.3. Peak voltage values observed during linear sweep voltammetry tests performed at different temperatures from $V = 3.00$ V → 0.02 V.................................................................152

Table 5.5. Diffusion coefficients of Li-ion ($D_{Li^+}$) at different temperatures obtained using the Randles-Ševčík method (Eq.5.1)................................................................................................................152

Table 6.1. Peak comparative elemental composition analyses using XPS of graphite electrode surfaces in Fig.6.6. Graphite electrodes were pre-treated in 1.0 wt.% Li$_2$CO$_3$-containing aqueous solution........................................................................................................183
LIST OF FIGURES

Chapter 1

Fig.1.1. Comparison of the gravimetric and volumetric energy densities of rechargeable battery systems [1].

Fig.1.2. (a) Theoretical maximum specific capacity and (b) volume changes in carbon, silicon and tin anodes during lithium insertion/de-insertion.

Fig.1.3. Schematic illustration of the charge/discharge process in a lithium-ion cell.

Fig.1.4. Stacking sequence in (a) hexagonal graphite [32] and (b) rhombohedral graphite [32].

Fig.1.5. XRD patterns of four graphite samples showing (a) a change in the spectra due to increase in the rhombohedral (3R)-phase content from the bottom (0%) to top (30%), and (b) the effect of particle size of the 3R content (the graphite particle size is reduced by a factor of 10 from the bottom to top) [33].

Fig.1.6. (a) TEM image of a thin section of synthetic graphite showing the presence of a dislocation in the area within the white rectangle. Seven lines are marked on the left-hand side of the enclosed area and only six are marked on the right-hand side. The terminating extra half-line is line no.4. (b) Schematic diagram showing an edge dislocation of Burgers vector $[20\bar{2}0]$ in the hexagonal layer plane in graphite [40].

Fig.1.7. Schematic representation of the LiC$_6$ structure with the stacking sequences of lithium occupancy perpendicular to the basal plane [58].

Fig.1.8. Schematic of stage formation during lithium intercalation into graphite [65].

Fig.1.9. Potential vs. composition during lithiation/de-lithiation of a graphite electrode at the C/50 rate at ambient temperature [70].
Fig.1.10. First galvanostatic charge/discharge cycle of a graphite Timrex® E-SLX 50 electrode in a 1 M LiClO₄ + EC/DMC electrolyte [74].

Fig.1.11. XRD patterns of lithiated graphite prepared by the electrochemical reduction of graphite in 1 M LiClO₄ EC/DME (1:1 by vol.) [75].

Fig.1.12. Schematic presentation of ‘Polyhetero Microphase’ SEI [82].

Fig.1.13. FTIR spectra measured from lithiated-delithiated synthetic graphite particles in 3 EC-DMC 1:1 Li salt solutions, 1 M LiAsF₆, 1 M LiPF₆, and 0.75 M LiC(SO₂CF₃)₃ in the diffuse reflectance mode [14].

Fig.1.14. XPS carbon 1s peaks obtained from a graphite and a lithium electrode. The dashed lines are spectra measured after 30 s of Ar⁺ sputtering. Electrodes were treated in EC-DMC/LiAsF₆ 1 M solutions. The graphite electrode was lithiated-delithiated (for 1 cycle) before the measurement [14].

Fig.1.15. Various reduction patterns of EC on graphite [14].

Fig.1.16. SEM images of graphite powder electrodes in (a) pristine condition and (b and c) after 140 cycles at 25°C [20].

Fig.1.17. SEM picture of a heat-treated powdered graphite electrode material (TIMREX® SLX50) taken from a half-cell that was discharged galvanostatically at 10 mA/g to 0.3 V vs. Li/Li⁺ and stabilized potentiostatically at this potential for 2 days using 1 M LiPF₆ in EC:DMC (1:1 by wt.) as electrolyte [15].

Fig.1.18. SEM images of (a) pristine graphite electrode, SLX50 and (b) cycled SLX50 taken from a half-cell. The electrode was charged galvanostatically at 10 mA/g to 0.3 V vs. Li/Li⁺ and stabilized potentiostatically at this potential for 2 days using 1 M LiPF₆ in EC:PC 1:1 (w/w) as electrolyte. Exfoliated graphite layers were observed [16].
**Fig.1.19.** (a) SEM image of a pristine natural graphite sphere. Secondary electron FIB images of (b) the graphite sphere discharged to 0 V from OCV, and a (c) cross-sectional image obtained from a region marked in (b) showing the measurements of the SEI film [99].

**Fig.1.20.** In-situ Raman spectra measured at the indicated potentials from a single Timrex® synthetic graphite particle at the surface of a commercial negative electrode during the first charging at 0.1 mA/cm² in a 1 M LiClO₄ + EC/DMC electrolyte. The spectra were arbitrarily shifted on the vertical scale [74].

**Fig.1.21.** The first four cyclic voltammograms at a scan rate of 5 mV/s of a fresh HOPG basal plane in 1 M LiClO₄ in 1:2 (by wt.) EC:PC [57].

**Fig.1.22.** Contact mode AFM images of HOPG in 1 M LiClO₄ (1:2) EC:PC electrolyte. The scan size was 10×10 µm² and the image scan rate was 1 Hz. (a) At 3.0 V vs. Li/Li⁺; Δz = 10 nm (b) after 6 min at 0.005 V; Δz = 25 nm (c) after 41 min at 0.005 V; Δz = 15 nm (d) after 71 min at 0.005 V; Δz = 15 nm [102].

**Fig.1.23.** (a) In-situ AFM image showing the SEI formation in 1 M LiClO₄ + EC/DMC electrolyte on a step at the basal surface of a HOPG electrode. The image was recorded at one line per second during a 5.0 mV/s potential sweep from 1.3 to 0.0 V vs. Li/Li⁺. Vertical surface profiles from (a) where (b) corresponds to a potential of 0.25 V showing 15 nm high SEI islands, and (c) shows the surface profile recorded when SEI growth was completed (at 3.0 V after 2 cycles) [74].

**Fig.1.24.** SEM images of (a) the as-prepared Sn-carbon fibre electrode; (b) a cross section of a Sn-coated carbon fibre before cycling; (c) the carbon fibre electrode after 20 galvanostatic cycles; (d) a cross-section showing damage of the Sn coating [108].
Fig.1.25. Comparison of cycling characteristics of natural graphite electrodes with (a) PAN encapsulated graphite electrodes at a current density of 0.2 mA/cm$^2$ in PC-based electrolyte [109], and (b) PDMS-treated graphite at C/6 rate [110].

Fig.1.26. In situ system for observing reaction of a-Si$_{0.64}$Sn$_{0.36}$ composite electrodes with lithium [136].

Fig.1.27. A cell designed for in-situ AFM during electrochemical tests [136].

Fig.1.28. (a) In-situ AFM images of Sn$_{32}$Co$_{38}$C$_{30}$ electrochemically reacting with lithium. (b) The potential vs. time plot, each plateau corresponding to the potentials (a-i) in the AFM results in (a) [138].

Chapter 2

Fig.2.1. De-lithiation step in a cyclic voltammetry experiment, indicating variations in voltage and current density with time, performed between (a) 0.000 and 3.000 V at a linearly increasing scan rate of 2.00 mV/s with in-situ digital microscope images at 1000× showing the (b) initial condition, and after (c) 9 s, (d) 70 s, and (e) 820 s. Typical damage features are marked in Figs. 2.1(b) - (e).

Fig.2.2. Lithiation step in a cyclic voltammetry experiment, indicating variations in voltage and current density with time, performed between (a) 1.000 and 0.000 V at a linearly increasing scan rate of 500 µV/s with in-situ digital microscopy images at 1000× showing the (b) initial condition, and after (c) 380 s, (d) 900 s, and (e) 1380 s. Typical damage features are marked in Figs. 2.2(b) - (e).

Fig.2.3. (a) Cyclic voltammetry plot when high purity graphite electrode undergoes a complete cycle between 3.000 and 0.000 V at 2.00 mV/s scan rate. 3-dimensional digital microscope images show graphite surface at (b) initial condition (at 3.000 V), and changes after (c) 1200 s and (d) 1600 s.
Fig. 2.4. Schematic illustration of the damage related events in graphite when cycle starts with (a) de-lithiation (when extensive loss of graphite particles constituted damage) and (b) lithiation (when surface film formation prevented graphite damage). .....

Chapter 3

Fig. 3.1. Experimental set-up for in-situ observation of graphite surface damage in a lithium-ion cell using an optical microscope. .................................................................

Fig. 3.2. Cyclic voltammetry plots for graphite electrodes showing the first cycles performed between 0.0 and 3.0 V using scan rates of 50 μVs⁻¹, 100 μVs⁻¹ and 2 mVs⁻¹. ............

Fig. 3.3. SE-SEM images of graphite surfaces (a) before cycling showing the presence of natural cavities, and (b) after cycling between 0.0 and 3.0 V at a linear scan rate of 2 mVs⁻¹, revealing sites of cavities due to graphite particle removal (exfoliation). ..... 

Fig. 3.4. Plot showing calculated area percent of cavities formed on graphite surface at different voltage scan rates. The area percentage of the surface cavities were monitored for the initial 200 s of each experiment. The arrows show no further change in area percentage until the end of the test (1000 s). ..............................................

Fig. 3.5. SEM images illustrating the preparation steps of TEM sample by FIB “lift-out” method from a graphite electrode cycled between 0.0 and 3.0 V at a linear scan rate of 5 mVs⁻¹ for 50 cycles: (a) Two trenches are ion-milled at a specific location across the graphite surface to produce a thin lamella. (b) A micro-manipulator is positioned at the top of the region of interest in the lamella. (c) The tip of the micro-manipulator was welded to the membrane using a thin layer of carbon. (d) The sample is lifted out of the trench. .................................................................

Fig. 3.6. Cross-sectional SEM image of the subsurface region (marked in Fig. 3.5 (a)) of the graphite electrode cycled between 0.0 and 3.0 V at a linear scan rate of 5 mVs⁻¹,
showing the presence of cracks resulting in partial delamination of graphite layers at the SEI/graphite interface. .............................................................................................................87

**Fig.3.7.** (a) A low magnification, bright-field TEM image of the same region shown in Fig.3.6, at the SEI/graphite interface. (b) High-magnification bright-field TEM image obtained from a region, marked as (b) in (a), revealing a granular appearance of the electrode/electrolyte interface. SAED patterns obtained from (c) a region [marked as (c) in (a)] in bulk graphite, and (d) from a region [marked as (d) in (a)] in the SEI layers. .....................................................................................................................88

**Fig.3.8.** (a) Bright field TEM image of electrochemically cycled graphite from a region close to the interface [marked as AA' in Fig.3.7 (a)] revealing graphite layer delamination initiated with the formation of crack tips. (b) HR-TEM image of the region, indicated as (b) in (a), revealed the point of separation of two graphite layers (consisting of graphene planes) and depicted the root of a crack. A tilt was observed between the crack faces, which consisted of the (002) planes of graphite. (c) Reduced FFT-derived diffraction patterns confirming the presence of Li-C compounds only at the root of layer separation as seen in (a). ............................................................90

**Fig.3.9.** A high magnification BF-TEM image revealing the deposition of SEI layers at the crack tip, and a typical example of a delaminated graphite layer marked as B in Fig.3.7 (a) extending across the crack faces.................................................................92

**Fig.3.10.** A schematic showing the occurrence of mechanisms responsible for possible reduction in graphite crack growth; deposition of the co-intercalation compounds near the crack tip causing partial closure of crack, and crack face bridging by graphite fibres. ...............................................................................................................................93
Chapter 4

Fig. 4.1. (a) An SEM (FEI Quanta 200 FEG) image of a graphite electrode surface before cycling showing the presence of porosities. (b) An XRD spectrum of the electrode surface obtained using a Bruker-AXS D8 diffractometer set to grazing incidence mode (incident angle, \( \omega = 1^{\circ} \)). (c) 3-dimensional optical surface profilometry image of graphite electrode surface obtained using WYKO NT 1100, showing the surface morphology of the graphite.

Fig. 4.2. Plots of current density against voltage (vs. Li/Li\(^+\)) obtained from linear sweep voltammetry tests performed on graphite anodes from 3.00 V to 0.02 V at sweep rates from 0.05-5.00 mVs\(^{-1}\). The scan peaks, attributed to solvent reduction during each test, have been indicated by arrow marks. The voltage and current density values corresponding to each peak have been tabulated in Table 4.1.

Fig. 4.3. Back-scattered (BS)-SEM images with corresponding EDS elemental maps (with red indicating graphite, oxygen represented by yellow and chlorine by blue; color available in online version) depicting changes in graphite electrode surfaces cycled from 3.00 to 0.02 V at scan rates of ((a) and (b)) 0.05 mVs\(^{-1}\), ((c) and (d)) 0.10 mVs\(^{-1}\), and ((e) and (f)) 5.00 mVs\(^{-1}\). Oxygen is a component of LiClO\(_4\) (electrolyte salt), Li\(_2\)CO\(_3\) and Li\(_2\)O\(_2\) (formed during electrochemical reduction as reported in Section 4.3.3) and chlorine is a component of LiClO\(_4\).

Fig. 4.4. (a) FIB-milled, cross-sectional microstructure of a graphite electrode cycled from \( V = 3.00 \rightarrow 0.02 \) V at 0.05 mVs\(^{-1}\); (b) SEI deposits formed on the graphite surface at 0.05 mVs\(^{-1}\); (c) FIB-milled, cross-sectional microstructure of a graphite electrode cycled at 5.00 mVs\(^{-1}\) in the same range as (a), and (d) SEI deposits formed on graphite surface at 5.00 mVs\(^{-1}\).
Fig. 4.5. Raman spectra obtained from (a) pristine graphite and (b) the graphite electrode cycled between 3.00 and 0.02 V at a linear scan rate of 5.00 mVs⁻¹ for 50 cycles. Multiple low intensity peaks close to 950-1085 cm⁻¹ indicate the presence of Li₂CO₃ on the graphite surface.

Fig. 4.6. (a) Dark-field TEM image acquired using {100} diffraction beam of the (b) selected area diffraction pattern showing randomly oriented nanometer-sized graphite grains near the SEI/graphite interface. Diffraction spots corresponding to the {002} planes of graphite, {110} planes of Li₂CO₃ and {101} planes of Li₂O₂ were also observed. (Carbon was deposited during the TEM sample preparation prior to FIB-milling.)

Fig. 4.7. (a) A high magnification cross-sectional bright-field TEM image of a graphite electrode cycled between 3.00 V and 0.02 V at a scan rate of 0.05 mVs⁻¹ showing {002} graphite layers running parallel to each other and merging with the electrode/electrolyte interface. The SEI at the interface displayed a granular appearance. The {002} direction was determined by the orientation of the $g_{002}$ vector.

Fig. 4.8. Plot showing changes in the Li⁺ diffusion coefficient ($D_{Li^+}$), calculated based on the Randles-Ševčík relationship between peak currents ($i_p$) and the square root of potential scanning rates ($dV/dt$).

Fig. 4.9. Cross-sectional SEM image of the subsurface region of a graphite electrode showing the presence of cracks at the SEI/graphite interface.

Fig. 4.10. Schematic representation of the mechanisms of SEI formation and composition on graphite electrodes cycled at different scan rates.
Chapter 5

Fig. 5.1. Schematic representation of the experimental setup used for in-situ observation of graphite electrode surface in a Li-ion cell at elevated temperatures using an optical microscope. ................................................................. 133

Fig. 5.2. Plot showing the variation of planar capacity with the cycle number during tests conducted at 25, 50 and 60°C................................................................. 136

Fig. 5.3. Optical microstructures (at 1000×) of graphite electrodes obtained in-situ during
the first cycle scan from 3.00 V to 0.02 V at 25°C (a) at the beginning of the test (3.00 V) and after reaching (b) 1.00 V, (c) 0.50 V, (d) 0.02 V. Microstructures obtained during tests performed at 60°C for voltages at (e) 3.00 V (f) 1.00 V, (g) 0.50 V and (h) 0.02 V. The scan rate used during the linear sweep tests was 2.00 mVs⁻¹. Comparison of areas marked in the microstructures show enlargement of pre-existing pores and formation of cavities by removal of graphite particles..... 137

Fig. 5.4. (a) SEM image of the cross-sectional view of cavities formed on the graphite surface (Fig.5.3) as a result of fragmentation and delamination of graphite at 25°C. (b) Histogram showing the cavity size distribution on a graphite surface cycled at 25°C................................................................. 139

Fig. 5.5. Plot showing calculated area percent of cavities formed on graphite surface in the first cycle at different temperatures. The arrows show no further change in area percentage until the end of the test (1500 s)............................... 140

Fig. 5.6. (a) SEM image showing the morphology of the SEI layer formed on graphite at 25°C after the first cycle. (b) Cross-sectional microstructure of the SEI formed at 25°C. The SEI is porous and non-uniform. The interface between the W-layer
(deposited for protection against beam-induced damage) and the SEI is demarcated by a dotted line. ................................................................................................................................. 141

**Fig.5.7.** (a) SEM image showing the morphology of the SEI layer formed on graphite at 60°C after the first cycle. (b) Cross-sectional microstructure of the SEI formed at 60°C. The SEI is dense and uniformly covered the graphite surface. ................. 142

**Fig.5.8.** EDS elemental maps (with yellow indicating carbon, oxygen represented by red and chlorine by blue) depicting changes in graphite electrode surfaces after the first cycle (scan rate of 0.50 mVs⁻¹) at (a) 25°C and (b) 60°C. .................................................. 143

**Fig.5.9.** (a) Bright-field TEM image and EDS elemental line scans obtained from the SEI/graphite interface. (b) HR-TEM image showing crystalline domains of Li₂CO₃ and nano-fragments of graphite within the SEI. .......................................................... 144

**Fig.5.10.** EELS spectra of (a) lithium, (b) carbon and oxygen in the SEI formed at 60°C. 145

**Fig.5.11.** High-resolution XPS spectra (fitted Gaussian-shaped components) of graphite surface that recorded the binding energies of (a) C 1s after cycling at 25°C, (b) C 1s after cycling at 60°C, (c) Li 1s after cycling at 25°C, and (d) Li 1s after cycling at 60°C. The shift in the location of the Li-CO₃ group from 56.6 (at 25°C) to 55.4 eV (at 60°C) possibly occurred due to electrostatic charging of the SEI. .......................... 146

**Fig.5.12.** FTIR spectra obtained from graphite electrode surfaces tested at 25 and 60°C, and compared with reference spectra of Li₂CO₃ and LiClO₄. .................................................. 148

**Fig.5.13.** Plots of current density against voltage (vs. Li/Li⁺) obtained from cyclic voltammetry tests performed on graphite anodes between 3.00 V to 0.02 V (a) at different temperatures using a constant voltage scan rate of 5.00 mVs⁻¹, and (b) at a constant temperature of 60°C using different scan rates. .................................................. 151
Fig.5.14. (a) Plot showing changes in the peak current density ($i_p/A$) with the square root of potential scanning rates ($dV/dt$). Li-ion diffusion coefficient ($D_{Li^+}$) was calculated from the slope. (b) Temperature dependence of $D_{Li^+}$ at the electrode/electrolyte interface. ................................................................. 153

Fig.5.15. Schematic representation of the possible mechanisms of SEI formation at (a and b) 25°C and (c and d) 60°C. At 25°C, the slow rate of diffusion of Li-ions towards the interface led to the formation of a non-uniform SEI layer that was unable to protect the graphite surface from damage in the first cycle. A high diffusion rate at 60°C resulted in formation of a uniform SEI that could protect the graphite surface from damage. ................................................................................................. 156

Fig.5.16. Variation of planar capacity with the cycle number during tests conducted at 25°C (a) with and (b) without a thermal pre-treatment at 60°C. The effects of further thermal cycling are also shown. ..................................................................................... 158

Chapter 6

Fig.6.1. Experimental setup for in situ Raman spectroscopy of surface changes on graphite anodes installed in an electrochemical cell with glass window. Only the top surface of graphite was exposed to the electrolyte. See [10] that shows a similar setup for in situ optical microscopy. ............................................................................................................. 170

Fig.6.2. (a) Linear sweep voltammetry experiment performed using an untreated graphite electrode showing variation of current density between 3.00 and 0.02 V at a scan rate of 2.0 mV/s. Optical microstructures were obtained at 1000× showing (b) initial surface condition with some surface pores, and after (c) 1000 s, (d) 1250 s, (e) 1450 s, and (f) 1490 s. Slight overall contrast change indicates formation of SEI that
was unable to prevent graphite surface damage. The arrow marks the same location (an initial pore) during successive phases of the experiment. .......................... 173

**Fig.6.3.** (a) Linear sweep voltammetry experiment performed using a pre-treated graphite electrode (1.0 wt.% Li₂CO₃) showing variation of current density between 3.00 and 0.02 V at a scan rate of 2.0 mV/s. Optical microstructures were obtained at 1000× showing the (b) initial condition, and after (c) 1000 s, (d) 1250 s, (e) 1450 s, and (f) 1490 s. The SEI could reduce graphite surface damage. The arrow marks the same location (an initial pore) during successive phases of the experiment. ............... 175

**Fig.6.4.** *In situ* Raman spectra obtained from (a) untreated and (b) pre-treated (1.0 wt.% Li₂CO₃) graphite electrodes when scanned from 3.00→0.02→3.00 V at a linear scan rate of 2.0 mV s⁻¹. (c) Plot showing changes in the position of the G-band observed in the Raman spectra obtained from untreated and pre-treated graphite electrode surfaces. ........................................................................................................................................................................ 177

**Fig.6.5.** Change in planar capacity of untreated graphite electrodes and electrodes subjected to Li₂CO₃ surface pre-treatments with number of cycles............................................................ 180

**Fig.6.6.** High-resolution XPS spectra showing the binding energies of C 1s obtained before cycling from (a) pre-treated graphite surface (1.0 wt.% Li₂CO₃), and after cycling of (b) untreated and (c) pre-treated (1.0 wt.% Li₂CO₃) graphite surfaces. ............................... 182

**Fig.6.7.** FTIR spectra measured from pre-treated graphite electrode surfaces (1.0 wt.% Li₂CO₃) (a) before cycling and compared with the reference spectra of Li₂CO₃; (b) after cycling and compared with spectra obtained from untreated graphite electrode surfaces, Li₂CO₃ and LiClO₄................................................................. 185

**Fig.6.8.** (a) High-resolution TEM image of the SEI formed on Li₂CO₃-treated graphite electrode showing the existence of randomly-oriented Li₂CO₃ crystals of size
14.6±6.9 nm. (b) An electron diffraction pattern obtained from a region (diameter = 60 nm) within the SEI layer shows diffraction rings with strong intensity corresponding to crystallographic planes of Li₂CO₃, along with weaker rings of graphite planes indicating the presence of graphite fragments.

**Fig.6.9.** High-resolution TEM images of (a) the SEI formed on Li₂CO₃-treated graphite and (b) untreated graphite electrodes. FFT-derived diffraction pattern (inset) of a marked crystalline domain suggested the presence of Li₂CO₃ and graphite fragments within the SEI formed on untreated electrodes.

**Fig.6.10.** Schematic representation of the mechanisms of SEI formation and Li⁺ diffusion in untreated and pre-treated graphite surfaces. (a) The SEI formed on untreated graphite surfaces was unable to prevent damage by graphite fragmentation and crack growth. (b) After prolonged cycling, the capacity dropped considerably due to inferior Li⁺ diffusion through the SEI. (c) However, the SEI layer formed in presence of Li₂CO₃ particles deposited on graphite surface prior to cycling prevented electrode damage in the first cycle; (d) the SEI assisted in enhanced Li⁺ diffusion and, hence, improved planar capacity.

**Chapter 7**

**Fig.7.1.** (a) SEM image of carbon fibres before coating; (b) high magnification SEM image of the region marked as (b) in (a) showing the fibre’s surface texture; (c) SEM image of Sn-coated fibres; (d) high magnification SEM image of the equi-axed Sn grains present in the region marked as (d) in (c).

**Fig.7.2.** (a) Cross-sectional STEM image of a single layer of Sn grains across the coating thickness; (b) HR-TEM image obtained from a location (marked as (b) in (a)) at the fibre/Sn interface.
Fig.7.3. Variation of planar capacities of the Sn-CFP composite, pure Sn and the CFP electrodes with cycle number. ................................................................. 209

Fig.7.4. (a) SEM image of the Sn-CFP electrode in as-prepared condition. (b) EDS map of the area shown in (a) with C shown as yellow and Sn shown as purple. (c) Back-scattered SEM image of the Sn-CFP electrode microstructure after 20 cycles. (d) EDS map of the area shown in (c). ................................................................. 210

Fig.7.5. SEM images showing (a) uncoated and (b) Sn-coated fibres after cycling. ....... 211

Fig.7.6. (a) A cross-sectional STEM image showing Sn-coated carbon fibres after cycling having clustered and isolated Sn particles scattered in a porous matrix. (b) HR-TEM image of disintegrated Sn nanoparticles in the amorphous matrix. Inset shows a FFT-derived diffraction pattern indicating the co-existence of Sn and Li₂CO₃. 213

Fig.7.7. Optical micrographs obtained in situ at 1000× during CV experiments with Sn-coated CFP electrodes: (a) at the beginning of the test (3.00 V), after (b) 1 cycle, (c) 10 cycles, (d) 19 cycles, (e) 28 cycles and (f) 42 cycles. ............................................... 215

Fig.7.8. A series of Raman spectra obtained in situ during CV experiments with Sn-coated CFP electrodes. Increase in the G-band (1581 cm⁻¹) peak intensity after 19 cycles indicated disintegration of the Sn coating and exposure of the CFP substrate. ..... 217

Fig.7.9. The d-spacing values of the graphite (002) planes in the carbon fibres for the CFP and the Sn-coated CFP anodes measured along the radius of the fibres before and after the electrochemical cycling. ................................................................. 218

Fig.7.10. Schematic diagram showing the capacity fading mechanisms of Sn-coated, bulk Sn and uncoated CFP anodes. The increased capacity of Sn-CFP in Stage 1 was due to their large surface area compared to bulk Sn electrodes. The low rate of capacity fading of Sn-CFP in Stage 2 was attributed to protection of the fibres by the Sn-
coating. In Stage 3, the capacity declined rapidly since electrochemical cycling caused disintegration of the coating. In comparison, ‘mud crack’ formation in bulk Sn and exfoliation of uncoated fibres would lead to a high capacity fading rate immediately after Stage 1.

Chapter 8

Fig.8.1. Electrode damage map of polycrystalline graphite electrodes cycled in EC-containing electrolyte.

Fig.8.2. SEM images showing MCMB particles (a) before cycling, and (b) after cycling in EC- and (c) PC-based electrolytes.

Fig.8.3. Cross-sectional SEM images of MCMB particles obtained after cycling in (a) EC- and (b) PC-based electrolytes. (c) A bright-field TEM image showing the morphology of the SEI layer formed on an MCMB particle.

Fig.8.4. Optical microstructures obtained in-situ at 1000× in EC-electrolyte (a) before the test, after (b) the first and (c) the fifth cycles, and in PC-electrolyte (d) before the test, and after (e) the first, and (f) the fifth cycles.

Fig.8.5. 3-dimensional optical profilometry images of a Si particle obtained at 20× (a) before cycling and (b) after cycling in EC-electrolyte for five cycles. (c) Comparison of 2-dimensional profiles of the same particle obtained before and after cycling.

Fig.8.6. 3-dimensional optical profilometry images of a Si particle obtained at 20× (a) before cycling and (b) after cycling in PC-electrolyte for five cycles. (c) Comparison of 2-dimensional profiles of the same particle obtained before and after cycling.

Fig.8.7. In situ micro-Raman spectra obtained from Si during the first and second cycles in EC-electrolyte.
# LIST OF ABBREVIATIONS/SYMBOLS

## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BHT</td>
<td>Butylated Hydroxytoluene</td>
</tr>
<tr>
<td>BS-SEM</td>
<td>Back Scattered Scanning Electron Microscopy</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>CFP</td>
<td>Carbon Fibre Paper</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl Carbonate</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-Dimethoxy Ethane</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene Carbonate</td>
</tr>
<tr>
<td>EDM</td>
<td>Electric Discharge Machining</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Ordered Pyrolytic Graphite</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>High Resolution Transmission Electron Microscope</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear Sweep Voltammetry</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>MCMB</td>
<td>Mesocarbon Microbead</td>
</tr>
<tr>
<td>Nd-YAG</td>
<td>Neodymium-doped Yttrium Aluminum Garnet (Nd:Y₃Al₅O₁₂)</td>
</tr>
<tr>
<td>Ni-Cd</td>
<td>Nickel-Cadmium</td>
</tr>
<tr>
<td>Ni-MH</td>
<td>Nickel-Metal Hydride</td>
</tr>
<tr>
<td>OCP</td>
<td>Open Circuit Potential</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene Carbonate</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>SADP</td>
<td>Selected Area Diffraction Pattern</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid Electrolyte Interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SE-SEM</td>
<td>Secondary Electron Scanning Electron Microscopy</td>
</tr>
<tr>
<td>Sn-CFP</td>
<td>Tin coated Carbon Fibre Paper</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>XHR-SEM</td>
<td>Extreme High Resolution Scanning Electron Microscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
</tbody>
</table>
# Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$</td>
<td>Activation Energy</td>
</tr>
<tr>
<td>$a$</td>
<td>Crack length</td>
</tr>
<tr>
<td>$A$</td>
<td>Electrode area</td>
</tr>
<tr>
<td>$C_{i,i}$</td>
<td>Concentration of the electro-active species in the electrolyte</td>
</tr>
<tr>
<td>$da/dN$</td>
<td>Crack extension rate</td>
</tr>
<tr>
<td>$\Delta K$</td>
<td>Cyclic stress intensity factor</td>
</tr>
<tr>
<td>$D_{Li^+}$</td>
<td>Diffusion coefficient of Li$^+$</td>
</tr>
<tr>
<td>$\Delta V$</td>
<td>Potential difference</td>
</tr>
<tr>
<td>$dV/dt$</td>
<td>Voltage scan rate</td>
</tr>
<tr>
<td>$\Delta V_{crit}$</td>
<td>Critical potential difference</td>
</tr>
<tr>
<td>$i_p$</td>
<td>Peak current</td>
</tr>
<tr>
<td>$i_p/A$</td>
<td>Peak current density</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of electrochemical cycle</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons transferred in the electrode reaction</td>
</tr>
<tr>
<td>$V_{crit}$</td>
<td>Critical voltage</td>
</tr>
<tr>
<td>$V_p$</td>
<td>Peak voltage</td>
</tr>
</tbody>
</table>
CHAPTER 1: Research Background

1.1. Introduction

Li-ion batteries are highly efficient electrochemical energy storage systems used in a wide range of applications including mobile electronic devices and electric vehicles. Li-ion batteries are used due to the amount of energy they can store and their rate of charge/discharge. These two performance characteristics are commonly known as energy density (specific energy) and power density (specific power). Depending on the application, these energy and power densities are either normalized to a weight (gravimetric) or a volume (volumetric). Batteries that are designed to fit in a certain space are characterized by their volumetric energy and power densities. When the battery weight is more critical, gravimetric energy and power densities are useful. Li-ion batteries are used for their higher volumetric (smaller) and gravimetric (lighter) energy densities compared to conventional battery systems like Ni-MH, Ni-Cd, Pb-acid, etc. as shown in Fig.1.1 [1].

![Fig.1.1. Comparison of the gravimetric and volumetric energy densities of rechargeable battery systems [1].](image-url)
The higher energy densities of Li-ion batteries are due to higher cell voltages (~3.7 V) achievable by the use of liquid electrolytes in an organic solvent, which also allow a wider temperature of operation. The specifications of Li-ion and other battery systems, along with their merits and demerits, have been presented in Table 1.1.

Table 1.1 – Characteristics of commonly used rechargeable batteries.

<table>
<thead>
<tr>
<th>Specifications</th>
<th>Pb-Acid</th>
<th>Ni-Cd</th>
<th>Ni-MH</th>
<th>Li-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Voltage (V)</td>
<td>2.0</td>
<td>1.2</td>
<td>1.2</td>
<td>3.7</td>
</tr>
<tr>
<td>Specific Energy Density (Wh/Kg)</td>
<td>30-50</td>
<td>45-80</td>
<td>60-120</td>
<td>150-190</td>
</tr>
<tr>
<td>Cycle Life (80% discharge)</td>
<td>200-300</td>
<td>1000</td>
<td>300-500</td>
<td>500-1000</td>
</tr>
<tr>
<td>Merits</td>
<td>• Low cost</td>
<td>• Long cycle life</td>
<td>• High energy density</td>
<td>• Very high energy density</td>
</tr>
<tr>
<td></td>
<td>• High rate capabilities</td>
<td>• Good storage characteristics</td>
<td>• Environmentally friendly</td>
<td>• Good storage characteristics</td>
</tr>
<tr>
<td>Demerits</td>
<td>• Low energy density</td>
<td>• Low energy density</td>
<td>• Requires overcharge/discharge protection</td>
<td>• High cost</td>
</tr>
<tr>
<td></td>
<td>• Potential health risks</td>
<td>• Potential health risk</td>
<td></td>
<td>• Potential health risks</td>
</tr>
</tbody>
</table>

In the near future, the efficient utilization of energy will be a major challenge. Regenerative braking systems help to lower consumption in hybrid vehicles and reduce their carbon footprint. They can also increase the range of electric vehicles, making them suitable for everyday use. In a battery-powered electric vehicle, regenerative braking is the conversion of the vehicle’s kinetic energy into chemical energy stored in the battery, where it can be used later to drive the vehicle. During regenerative braking, the charging current is very high and the diffusion rate of lithium-ions towards the graphite electrode in the battery exceeds the rate at which the ions can be intercalated into the graphite electrode. Under these
conditions, the accelerated diffusion of lithium-ions at the electrode/electrolyte interface would lead to an ‘electrochemical shock’ [2,3] resulting from strain-induced damage of the graphite anode. Gradual degradation of the anode material causes a decline in the battery capacity and cycle life.

One of the most challenging aspects of the Li-ion battery design is to reduce capacity fading and impedance growth. Capacity fade refers to the loss in discharge capacity that a battery demonstrates over time. The loss in discharge capacity occurs whether the battery is inactive (“calendar life” losses) or exercised (“cycle life” losses). The factors contributing to capacity fade also assists in impedance growth. Impedance growth is caused by resistance to ion and electron transport in the various components of the battery. Impedance growth leads to a reduction in the rate capability of the battery. Li-ion batteries using graphite anodes experience solid electrolyte interphase (SEI) growth that increases the impedance during battery aging. Electrode degradation and the loss of active material cause a decrease in the available surface area for reactions and, therefore, results in higher impedance.

Thus an ideal anode material in lithium-ion batteries should (i) have high specific energy capacity, (ii) resist mechanical degradation when lithium is inserted/removed, and (iii) prevent SEI growth and lithium plating on the anode/electrolyte interface [4]. Graphite is the ‘standard’ material for lithium-ion battery anodes, as it is relatively insensitive to electrolyte and has a lower tendency to mechanical instability than pure lithium, but has a low energy capacity. In general, elements like P, As, Sb, Bi, and Sn that have the ability to react reversibly with large amounts of lithium provide high anode potentials but suffer from large cyclic volume changes that make them susceptible to mechanical degradation. Currently, no sound material design method exists to make rational selections for durable
anodes. Extensive work continues to find new anode materials [5], but these attempts are guided by iterative processes rather than a firm design criterion. Developing new microstructural and surface engineering methods for manufacturing durable anode materials is the research of the future; a process to develop a unique design criterion that can be used for anode material selection. In general, the anode design strategy should be based on alloying high charge capacity elements with inactive elements that are less prone to degradation. Hence, understanding degradation and damage mechanisms that occur in negative electrodes (anodes) of Li-ion batteries during intercalation (Li-ion insertion)/de-intercalation cycles is of key importance.

Graphite, with a theoretical charge capacity of 372 mAh/g [Fig.1.2 (a)], is the preferred anode material [6] and undergoes a volume change of only 12% during electrochemical cycling, which is much less than other anode materials like Sn and Si [Fig.1.2 (b)]. The latter has very high capacity of 4200 mAh/g, but undergoes a massive volume expansion of 400% [7] that leads to rapid mechanical disintegration [8-10]. Yet, graphite electrodes suffer from mechanical degradation and there is increasing evidence that it is this instantaneous damage that is largely responsible for graphite's irreversible charge loss and capacity drop during the first cycle [11,12]. The damage in the first cycle is thought to cause by a fragmentation process that occurs by means of detachment of graphite particulates [13-17]. After the first cycle, the decrease in the capacity continues but at a much slower rate. The gradual capacity loss is thought to be caused due to graphite exfoliation during which the graphene layers become delaminated. Several experimental [18-21] and theoretical [22-24] studies have been undertaken to determine the roles of intercalation/de-intercalation induced stresses on the graphite lattice. The role of electrolyte species (e.g., Li_x(solvent)_yC_n) that co-intercalate between graphene layers have also been noted using atomic force
microscopy and Raman spectroscopy [25]. Optical microstructural investigations that provide microscopic evidence for degradation due to lithiation of graphite [26] and Si based (Si-Sn) electrodes [27-29] have also been reported.

![Bar chart showing theoretical specific capacity and volume changes in carbon, silicon, and tin anodes](image)

Fig.1.2. (a) Theoretical maximum specific capacity and (b) volume changes in carbon, silicon and tin anodes during lithium insertion/de-insertion.

An important aspect of the electrode degradation process is the formation of SEI on electrode surfaces. As the organic electrolytes are not stable at low potentials typically below
0.8 V, they decompose to form the SEI [24]. It was suggested that SEI would inhibit the reaction of electrolyte with the electrode material [25]. Consequently they are considered protective layers that reduce the rate of graphite exfoliation [26-29]. However the details of compositions, microstructures, and morphologies of SEI remain to be better understood. Dynamic changes in the SEI's components can occur depending on the temperature and voltage scan rates. These factors also influence the severity of electrode degradation.

Therefore, the objective of the literature survey is to understand the following aspects that have been previously reported:

1. Structure of graphite and the process of lithium intercalation into carbonaceous anodes.
2. SEI formation mechanisms based on spectroscopic observations.
3. Probable reasons of cycling-induced graphite damage.
4. In-situ observations of changes on graphite surface during electrochemical cycling.
5. Effect of surface modification and temperature on the electrochemical behaviour of carbonaceous anodes.
6. Application of alternative anode materials made from tin and silicon alloys.

1.2. Working Principle of a Lithium-ion Battery

A battery is composed of several electrochemical cells that are connected in series and/or parallel to provide the required voltage and capacity, respectively. Each cell consists of a positive and a negative electrode (sources of chemical reactions) separated by an electrolyte solution that enables ion transfer between the two electrodes. Once these electrodes are connected externally, the chemical reactions proceed in tandem at both the electrodes, thereby liberating electrons and enabling the current to be tapped by the user.
The lithium-ion cells are presently made with LiCoO$_2$ positive electrodes or cathodes and carbon anodes as shown in Fig. 1.3. In such a cell, Li-ions migrate from LiCoO$_2$ cathode to the Li$_x$C$_6$ anode through the electrolyte and the electron flows through the external circuit from the cathode to the anode during the charge process. An exactly reverse reaction occurs during the discharge process. Although the replacement of metallic lithium (having a huge capacity of 3860 mAh/g) by carbon (having a capacity of 372 mAh/g) causes an important sacrifice in energy density, the Li-ion cells involving the shuttling of Li-ions between the two insertion hosts without any metallic lithium, solve the dendrite problem and offer significant advantages in terms of safety and cycle life in comparison to Li-metal batteries. To compensate for the increase in potential of the anode, high-potential insertion compounds
are needed as the cathode. Since the graphite negative electrode does not contain lithium prior to testing in a battery, the cathode must act as a source of lithium, thus requiring use of air-stable lithium-based intercalation compounds to facilitate the cell assembly. LiCoO₂ is most widely used in commercial Li-ion batteries, deintercalating and intercalating lithium around 4 V.

1.3. Structure of Graphite

Since the determination of the structure of graphite by Bernal [30], more detailed studies of natural and artificial graphites prepared by a variety of methods and from a variety of starting materials have been undertaken. Although the classical structure described by Bernal is still the prototype for all graphite structures, variations exist and they manifest themselves in modified X-ray diffraction patterns. The usual hexagonal layer stacking (2H) of pristine graphite is -ABAB- as shown Fig.1.4 (a). Lipson & Stokes [31] described the rhombohedral form (3R) with -ABCABC- layer stacking [Fig.1.4 (b)], instead of the -ABAB- layer stacking of the classical form.
Fig.1.4. Stacking sequence in (a) hexagonal graphite [32] and (b) rhombohedral graphite [32].

In both phases, the carbon-carbon distance within each layer is 0.14 nm, and the interlayer spacing is 0.34 nm. Fig.1.5 (a) [33] shows X-ray diffraction (XRD) patterns obtained from graphite samples with different phase ratio of 2H and 3R. The 3R phase contents for the graphite samples were 0, 5, 19 and 30%, respectively, from the bottom to top. The (100) and (101) peaks obtained from the pure 2H phase graphite were clearly separated with no additional peaks nearby for 2θ between 40° and 50°. For the sample with 30% 3R content, the (101) and (101) peaks were prominent and their relative intensities were comparable with those of the 2H (100) and (101) peaks. On mechanical grinding, 2H graphite can be transformed into 3R. Fig.1.5 (b) shows the effect of reducing the graphite particle size on the 3R phase concentration. The bottom-most spectrum was obtained from a graphite sample with particle size of approximately 75 μm. From the bottom to the top,
the average graphite particle size is reduced by a factor of 10. It can be seen that the 3R peaks’ intensities increased with the decrease in the graphite particle size.

![Fig.1.5. XRD patterns of four graphite samples showing (a) a change in the spectra due to increase in the rhombohedral (3R)-phase content from the bottom (0%) to top (30%), and (b) the effect of particle size of the 3R content (the graphite particle size is reduced by a factor of 10 from the bottom to top) [33].](image)

The phase conversion could cause turbostratic disorder into the graphite structure that randomizes the stacking sequence of the parallel layers [34]. An increase in the disorder also causes an enthalpy difference between the 2H and 3R phases, \( \Delta H = H_{2H} - H_{3R} = 0.6 \) kJ/mol [34]. In summary, the 2H phase in graphite is thermodynamically more stable at normal temperature and pressure than the 3R phase. The slight energy difference between the 2R and 3H structures under normal conditions induces a smaller electrochemical potential difference amongst the two phases.

In a study of natural and synthetic graphites, Franklin [35,36] and Bacon [37,38] have shown that in addition to the modification of layer stacking which gives rise to the 3R form,
local changes in the stacking and arrangement of the 2H layer in graphites produce considerable variations in lattice parameters. In order to observe the changes in the stacking sequence in graphite, high-resolution electron microscopy studies have been conducted. TEM analyses were performed by Grenall [39] who reported dislocation movement in smeared flakes of natural graphite. Dawson and Follett [40] noted edge dislocations in thin sections of synthetic graphite that were observed as terminating extra half-lines in the moiré patterns [Fig.1.6 (a)]; these dislocations were present in the hexagonal layer net planes themselves and indicated that there was in this region a considerable deformation of the benzenoid structure of the hexagonal layer nets [Fig.1.6 (b)]. Horn [41] reported growth spirals on certain natural graphite crystals, but the density of these screw dislocations was
very low. Willamson [42] studied dislocations in a variety of single-crystal flakes of graphite using transmission electron microscopy (TEM). Dislocations occurred as pairs, approximately 1000 Å apart, with Burgers vectors of the type \( \frac{1}{3}a[1 \overline{1} 0] \) giving together a unit lattice translation of \( a \) along one of the three coplanar hexagonal axes. The area between these two partials contained a stacking fault. The stacking fault energy was calculated as 0.1 erg/cm\(^2\) and independent of temperature up to 900°C.

1.4. Lithium Intercalation in Graphite

The excellent electronic and ionic conductivities, low electrochemical voltage vs. Li/Li\(^+\), etc. make graphite a very attractive candidate as an anode material for rechargeable lithium-ion batteries [43]. The use of a graphite-based rechargeable cell was suggested by Rüdorff and Hoffmann as early as 1938 [44]. From an application point of view, lithium intercalated graphite was proposed as an anode material by Armand and Touzain [45]. Intercalation in graphite has been described as insertion of atomic or molecular layers of a different chemical species between the carbon layers that may result in a volume change perpendicular to the layers. The insertion process is reversible and “topotactic”, implying that the intercalation leads to a different inter-layer distance though the carbon atomic arrangement remain unchanged within the layer [46]. Graphite possesses a suitable structure for the diffusion of ionic, atomic and molecular species between the layers in order to form intercalation compounds. Intercalation in graphite has been studied by various researchers [47-50]. A variety of intercalants have been used and their chemical and physical properties such as electrical, thermal and magnetic behavior have been studied [48,51-54]. Lithium intercalation experiments on graphite have been performed using natural graphite flakes and highly oriented pyrolytic graphite (HOPG). The common intercalation methods are
Considerable efforts have been undertaken to study lithium intercalation leading to the nominal composition \( \text{Li}_x\text{C}_6 \) with \( 0 \leq x \leq 1 \). Electrochemical intercalation of graphite with lithium was achieved using non-aqueous electrolytes consisting of lithium salts such as lithium perchlorate and lithium triflate [55]. Tran and Kinoshita studied lithium intercalation perpendicular and parallel to the graphene layers [56,57].

**Fig. 1.7. Schematic representation of the \( \text{LiC}_6 \) structure with the stacking sequences of lithium occupancy perpendicular to the basal plane [58].**

In graphite, individual graphene sheets are composed of strong covalently bonded carbon atoms forming a honeycomb network. However, the only binding forces between the graphene sheets are due to the weak Van der Waals interactions. It has been suggested that during the lithium intercalation, the lithium occupies the sites between two adjacent graphene planes and, within a plane, each lithium is associated with a hexagonal carbon ring in such a way that the nearest neighbour occupation (corresponding to the maximum
composition LiC₆) is avoided as can be seen in Fig.1.7 [58]. Intercalation of lithium into graphite proceeds via a mechanism known as staging in which lithium completely intercalates into distant graphene layers before occupying neighbouring graphene layers. The staging phenomenon can be described by stage index, which is given by the number of unoccupied graphene layers between two occupied guest layers [59]. Fig.1.8 shows a scheme of this process that involves work to expand the Van der Waals gap between the graphene layers and repulsive interaction between the guest species [59]. As lithium intercalates, the hybridization between the lithium valence electrons and graphite interlayer states, although weak in nature [60], perturb and screen the carbon-carbon Van der Waals bonds, that is demonstrated by the change from -ABAB- hexagonal stacking in graphite to -AAAA- stacking [61-63]. Theoretical studies by Boehm [64] showed that the fully intercalated structure of graphite changes to -AAAA- stacking as shown in Fig.1.8. Thus, the nature and strength of the interlayer bonding in the lithium-graphite system changes as a function of increasing lithium content as there is an increase in the number of Li-C bonds and a corresponding decrease in the carbon-carbon Van der Waals interactions.

Fig.1.8. Schematic of stage formation during lithium intercalation into graphite [65].
In fully intercalated graphite, the lithium occupies the neighbouring gap between the graphene layers forming a Li-C\textsubscript{6}-Li-C\textsubscript{6} sequence along the c-direction (Fig.1.8). According to high-resolution TEM studies by Song et al. [66], the interplanar distance for x=1 in Li\textsubscript{1}C\textsubscript{6} increased to 0.37 nm in comparison with 0.34 nm for x=0. Shi et al. showed that both 3R as well as 2H phases were able to reversibly intercalate lithium resulting in similar intercalation capacities [33,67]. The electrochemical intercalation of lithium into a two-phase graphite mixture can be determined using the following assumptions. (i) The graphite contains a fraction, x, of the 3R phase and a fraction, 1-x, of the 2H phase, and that (ii) the intercalation rates are identical. Thus the electrochemical intercalation of lithium into the two-phase graphite can be described as [33],

$$\text{Li}^+ + 6\text{C} + e^- \rightarrow x\text{LiC}_6^{3R} + (1-x)\text{LiC}_6^{2H} \quad (1.1)$$

where, $C_{3R}$ and $C_{2H}$ represent 3R and 2H phase graphite, respectively. The total lithium intercalation capacities into a two-phase graphite, $C_{Total}$, is the sum of the lithium capacity in the 3R phase, $C_{3R}$, and that in the 2H phase, $C_{2H}$,

$$C_{Total} = C_{3R} + C_{2H} \quad (1.2)$$

It is assumed that an ideally fully lithiated 2H graphite comprises of alternating layers of carbon and lithium layer that results in a maximum theoretical capacity of 372 mAh/g (one lithium per six carbons, or LiC\textsubscript{6}). However, the maximum capacity is rarely attained experimentally due to the presence of turbostratic stacking disorder in most graphite structures.
1.5. Electrochemical Behavior of Graphitic Carbons with Lithium

It was seen in Section 1.4 that the interaction of lithium with carbonaceous materials could cause staging. Using first-principles investigations, Ceder et al. [68] suggested that the staging is a consequence of the competition between the lithium-lithium repulsive interactions and the carbon-carbon attractive Van der Waals interactions. Lithium that enters the graphite structure is not homogenously distributed between all the graphene layers at ambient temperatures. Instead, the lithium resides in certain interlayer ‘galleries’ depending upon the total amount of lithium present. The number of graphene layers present between those containing the Li-ions describes the distribution. The stage-1 structure has lithium between all the graphene layers. In stage-2, an empty gallery is present between each occupied gallery whereas in stage-4, four graphene layers exist between each gallery containing lithium.

A typical charge-discharge curve is shown in Fig.1.9. It can be seen that there is a difference between the data during charge, when lithium is being added, and discharge, when lithium is being deleted. The displacement (hysteresis) between the charge and the discharge curves has been attributed to the 8-22% irreversible charge loss in the first cycle [69] as well as the mechanical energy involved in the structural changes [70]. It can be seen in Fig.1.5 that the data show plateaus indicating the presence of composition ranges within which reconstitution reactions take place. As the composition changes along these plateaus, the stacking of graphene layers in different regions or domains will vary. The differences in stacking cause differences in interlayer spacing and, therefore, considerable amount of distortion or damage of the structure [71].
The irreversible charge consumption occurring during the first cycle of a graphite electrode cycled against metallic lithium was studied by Novak et al. [72-74]. A model was proposed to distinguish three types of irreversible charge consumption according to Fig.1.10: (i) the irreversible change related to the reduction of the surface groups of graphite between 3 and 0.8 V vs. Li/Li$^+$, (ii) the irreversible charge due to SEI formation by electrolytic decomposition between 0.8 and 0.2 V, and (iii) the irreversible charge due to reactions parallel to the reversible intercalation/de-intercalation of lithium-ions that contribute to the SEI film growth. It can be seen from the plot in Fig.1.10 that the main contribution to the irreversible charge consumption is in the region (ii) where the SEI film is thought to form.
Fig. 1.10. First galvanostatic charge/discharge cycle of a graphite Timrex® E-SLX 50 electrode in a 1 M LiClO₄ + EC/DMC electrolyte [74].

The staging phenomenon during the electrochemical reduction of natural graphite in 1 M LiClO₄ and EC/DME (1:1 by vol.) was investigated using XRD [75]. At 0.17 mA/cm², the voltage dropped from 3.0 V to below 1.0 V in three regions characterized by changes in slope at 190, 95 and 65 mV. A sloping curve from 0.8 to 0.2 V was only observed during the first reduction of graphite. Based on the graphite sample weight, the capacity for the first reduction to 0 V was observed to be 390-420 mAh/g. To follow the structural changes during the reduction, XRD tests were carried out at several degrees of reduction and presented in Fig. 1.11. In region 0 to 50 mAh/g of reduction, no indication of a change in XRD data was recognized. The reduction of graphite to 0 V did not reveal a pure single
Fig. 1.11. XRD patterns of lithiated graphite prepared by the electrochemical reduction of graphite in 1 M LiClO₄, EC/DME (1:1 by vol.) [75].

Stage compound as determined by the XRD patterns. To obtain XRD data for a pure single-stage compound at 0 V, the graphite and lithium electrodes were short-circuited for 48 hours following the constant-current reduction to 0 V. From the XRD data, the lattice parameters were calculated to be $a_L = 0.43$ nm and $c_L = 0.37$ nm assuming a hexagonal lattice. These
values are consistent with those reported for the Stage-1 compound, LiC₆ [6]. The lattice parameters of natural graphite used in this study are a₀ = 0.42 nm and c₀ = 0.67 nm (space group; P6₃/mmc). From the graphite interlayer distance c₀ (=c₀/2 = 0.34 nm) and the lithium intercalate sandwich thickness c_L (=0.37 nm), the interlayer distance for the n-th stage compound was calculated using c_n = c_L + (n-1)c₀.

1.6. Mechanisms of SEI Formation

Using EIS, FT-IR, XPS, XRD and TEM results, it was suggested that the SEI layer mainly consisted of Li₂CO₃ and lithium alkylcarbonate [76,77]. It was also predicted that the SEI layer might contain polymer-like substances with repeating oxyethylene units similar to polyethylene oxide [78]. Novák et al. [74] suggested that during SEI formation, carbonate solvent(s) are reduced initially, forming ethylene gas, organic radicals, oligomers, and polymers. Subsequently, the SEI is formed on the surface via a nucleation and growth mechanism. This section describes how the steps involved in SEI formation are reported in the literature.

While analyzing the electrochemical behavior of alkali and alkaline earth metals in non-aqueous battery systems, Peled [79] proposed that the SEI is conductive for ions but insulating for electrons. With the rapid development of rechargeable lithium-ion batteries, identification and characterization of the SEI film formed on various anodes became more important since battery characteristics, like irreversible capacity loss and cycle life, are related to the formation and evolution of the SEI film. It is generally accepted that reduction of the electrolyte is primarily responsible for SEI layer formation, yet the mechanism and kinetics of this process is complex and persist as a subject of controversy.
Fig. 1.12. Schematic presentation of ‘Polyhetero Microphase’ SEI [82].

The structure, chemical composition, morphology of the SEI film and its correlation with the electrochemical performance of batteries has been studied using EIS, STM, AFM and XPS techniques [80,81]. Ogumi [78] suggested that the SEI is formed mainly by the decomposition of EC. Peled et al. [79] assumed that the reduction of electrolyte salt anions and solvents proceeds simultaneously and both organic and inorganic materials precipitate on the electrode as a mosaic of microphases. Ultimately, the SEI film could have a mosaic-type structure consisting of ‘polyhetero microphases’ as seen in Fig. 1.12 [82,83], where inorganic compounds may predominate in the inner part and organic compounds are usually formed on the outer part [81]. Studies on solvent co-intercalation in graphite received attention. Fong et al. [84] suggested that the SEI film, formed on commercially available calcines petroleum coke and graphite during galvanostatic tests, slows the rate of the
decomposition of the 1 M LiAsF₆ (in a 1:1 mixture by volume of PC and EC) by forming a physical barrier between the lithiated carbon electrode and the electrolyte. However, there remains unresolved issues regarding the mechanism of surface and near-surface changes in graphite that are associated with irreversible charge consumption during the initial cycles and also during the subsequent cell cycling.

![FTIR spectra](image)

**Fig.1.13.** FTIR spectra measured from lithiated-delithiated synthetic graphite particles in 3 EC-DMC 1:1 Li salt solutions, 1 M LiAsF₆, 1 M LiPF₆, and 0.75 M LiC(SO₂CF₃)₂ in the diffuse reflectance mode [14].

Fig.1.13 shows FTIR spectra measured from graphite particles taken from electrodes that were cycled in EC-DMC (1:1) solutions of LiAsF₆, LiPF₆ and LiC(SO₂CF₃)₂ [14]. The three spectra differ from each other in their general shape and relative peak intensities. However, most of them depicted absorptions that were attributed to the peaks of the EC reduction products, (CH₂OCO₂Li)₂ and CH₂CH₂. In addition to these products, reduction of
EC on graphite may also form polymers [85,86]. In addition to FTIR analyses, XPS studies of lithiated graphite electrodes suggested the presence of species with Li-C bonds in the SEI layers (C1s peaks of binding energies below 283 eV).

Fig.1.14. XPS carbon 1s peaks obtained from a graphite and a lithium electrode. The dashed lines are spectra measured after 30 s of Ar⁺ sputtering. Electrodes were treated in EC-DMC/LiAsF₆ 1 M solutions. The graphite electrode was lithiated-delithiated (for 1 cycle) before the measurement [14].

Fig.1.14 shows the carbon spectra of Li-graphite electrodes after being treated in EC-DMC/LiAsF₆ solutions [14]. The graphite electrode was lithiated-delithiated before the measurement. The peak assignments appearing in this figure are based on [87-89]. A possible EC reduction product which contains a Li-C bond is LiCH₂CH₂OCO₂Li. Based on FTIR and XPS observations, a reaction scheme of the possible reduction reactions of EC on graphite surfaces was proposed [14]. Fig.1.15 shows that the EC reduction product
(CH₂OCO₂Li)₂ may be formed either by disproportionation (formed by a single electron transfer to EC), or by a two-electron transfer that form CO₃²⁻, which further attacks nucleophilically another molecule of EC [90]. The common product in both the above reactions, CH₂CH₂, is liberated as ethylene gas.

![Diagram of various reduction patterns of EC on graphite](image)

**Fig.1.15. Various reduction patterns of EC on graphite [14].**

1.7. Electrochemical Cycling-induced Surface Changes of Graphite Electrodes

One of the first microscopy studies on electrode degradation was made by Markevich et al. [20] who used SEM imaging techniques to characterize composite graphite powder electrodes (KS-15 from Timrex Inc.) subjected to cyclic voltammetry (CV), electrochemical impedance (EIS) and differential self-discharging as a function of cycle number. It was suggested that repeated lithium-ion insertion/de-insertion could produce stress in the electrodes that led to graphite structure degradation and loss of active mass.
Fig.1.16. SEM images of graphite powder electrodes in (a) pristine condition and (b and c) after 140 cycles at 25°C [20].

Fig.1.16 shows SEM images of the surface morphology of pristine [Fig.1.16 (a)] and different locations of cycled electrodes [Figs.1.16 (b) and (c)] used in this study. In cycled electrodes, cracks appeared frequently [Fig.1.16 (b)], and the flakes were partially exfoliated forming cracks between the layers. It was suggested that the cracks are preferred locations for the reduction of the electrolytic solution components. Thus the SEM images were interpreted such that during reversible lithium insertion into graphite electrodes, mechanical stress developed which disintegrated the graphite structure. Changes in the graphite structure
could lead to capacity fading during long-term cycling of graphite electrodes at ambient temperatures. The capacity fading was attributed to the decrease in the number of the sites available for reversible lithium-ion intercalation/de-intercalation.

In other studies [15,91-93], graphite powders, heat treated in an inert gas atmosphere above 1300°C, were cycled using EC-based electrolyte systems. The SEM image shown in Fig.1.17 was taken from a discharged electrode cycled in EC/DMC electrolytes; the image indicates possible cracks on the graphite particles in the electrode. An increased irreversible charge loss observed for heat-treated graphite, in comparison to the untreated electrodes, was attributed to an increased electrode surface area due to exfoliation of the graphite layers.

![3 μm](image)

**Fig.1.17.** SEM picture of a heat-treated powdered graphite electrode material (TIMREX® SLX50) taken from a half-cell that was discharged galvanostatically at 10 mA/g to 0.3 V vs. Li/Li⁺ and stabilized potentiostatically at this potential for 2 days using 1 M LiPF₆ in EC:DMC (1:1 by wt.) as electrolyte [15].

Investigation of graphite surface damage in electrochemical cells was also conducted by Buqa et al. [16]. An SEM image [Fig.1.18 (a)] of the SLX50 graphite powder electrodes used in this study depicted ordered and compact graphene layers before cycling. The electrodes were galvanostatically charged to 0.3 V vs. Li/Li⁺, and subsequently stabilized...
potentiostatically at 0.3 V. Fig.1.18 (b) illustrates the exfoliated graphite after being
electrochemically reduced in 1M LiPF₆ 1:1 (by wt.) + EC/PC electrolyte. The separation
between the graphene layers increased as indicated in Fig.1.14 (b). The exfoliation of
graphite was attributed to the co-intercalation of solvents and Li-ions during the SEI
formation [94].

Fig.1.18. SEM images of (a) pristine graphite electrode, SLX50 and (b) cycled SLX50
taken from a half-cell. The electrode was charged galvanostatically at 10 mA/g to 0.3
V vs. Li/Li⁺ and stabilized potentiostatically at this potential for 2 days using 1 M
LiPF₆ in EC:PC 1:1 (w/w) as electrolyte. Exfoliated graphite layers were observed
[16].
It has been suggested that the SEI suppresses the electrode/electrolyte reaction [58] and acts as a protective layer that reduce the rate of graphite exfoliation [79,81]. The process of graphite surface passivation and SEI formation is irreversible and proposed to cause loss of charge, i.e., decreases the energy density of the electrochemical cell. It has been suggested that the SEI layer on the graphite surface would influence the cycling stability, high current rate performance as well as the safety of the cell [95,96] and, therefore, the thickness of the SEI is critical. The SEI thickness would depend on the surface-to-volume ratio of the graphite. So far, there is no general conclusion about the thickness of the SEI layer. The difference in thickness reported in the literature is due to the difficulties in direct observation of the SEI, the nature of the electroactive materials, electrolytes and electrochemical states selected in respective studies. Kong et al. [97] reported a 36 nm thick SEI film formed on the surface of HOPG by using a spectroscopic ellipsometer that monitored SEI formation on HOPG surface. Ellipsometric data interpretation was based on fundamental optics of polarized light propagation in stratified planar structures. Yazami [98] observed a 40-80 nm thick film on the surface of lithiated graphite fibers by SEM. Fong et al. [84] calculated a SEI thickness of 4-5 nm on anodes consisting of petroleum coke particles. Peled et al. [80] obtained the depth profile of the SEI formed on the basal and edge planes of HOPG by controlling the sputtering time of XPS and roughly estimated the SEI thickness. A 7 nm thick SEI was formed on the basal planes, whereas the thickness of the SEI formed on the edge planes was 35 nm. Focused ion beam (FIB) technique was used by Zhang et al. [99] to investigate the evolution of morphology and composition of the SEI film formed on the surfaces of natural graphite spheres after cycling in an electrolyte with composition 1 M LiPF$_6$ in EC/DMC (1:1 by vol.). The electrochemical cell was discharged to 0 V from the open circuit voltage (OCV). The cell was galvanostatically charged and discharged in the
voltage range of 0.001-2.500 V vs. Li/Li⁺ at a current density of 0.2 mAcm⁻² for 5 and 24 cycles. SEM image of a typical pristine natural graphite sphere is shown in Fig.1.19 (a). It can be seen that there are cracks and partially unattached flakes on the surface prior to cycling. Fig.1.19 (b) is the microstructure of a cycled graphite sphere discharged to 0 V from OCV. Fig.1.19 (c) shows the cross-section of the cycled graphite sphere obtained from a region marked in Fig.1.19 (b).

![SEM images of graphite spheres](image)

**Fig.1.19.** (a) SEM image of a pristine natural graphite sphere. Secondary electron FIB images of (b) the graphite sphere discharged to 0 V from OCV, and a (c) cross-sectional image obtained from a region marked in (b) showing the measurements of the SEI film [99].

The existence of the SEI film was identified according to the contrast difference in the cross-sectional images. The SEI film formed initially was rough in morphology [Fig.1.19
(b)], had a thickness in the range of 450 to 980 nm, a non-uniform composition and contained small splits on the surface [Fig. 1.19 (c)]. The large variation in thickness was because of the surface features of natural graphite spheres that consisted of both basal and edge planes along with surface cracks [Fig. 1.19 (a)]. After 5 electrochemical cycles, the gradually thickened SEI film displayed micro-pores and after 24 charge/discharge cycles, the thickness of the SEI film increased to 1600 nm and consisted of cracks. Table 1.2 summarizes the SEI thickness values that have been reported in the literature.

**Table 1.2 – SEI thickness as reported in the literature.**

<table>
<thead>
<tr>
<th>SEI Thickness (nm)</th>
<th>Electrolyte Used</th>
<th>Anode</th>
<th>Analytical Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>36 [76]</td>
<td>1 M LiClO₄ in EC:DMC (1:1)</td>
<td>HOPG</td>
<td>Ellipsometry</td>
</tr>
<tr>
<td>35 [63]</td>
<td>1 M LiPF₆ in EC:DEC (1:1)</td>
<td>HOPG</td>
<td>XPS</td>
</tr>
<tr>
<td>40-80 [77]</td>
<td>1 M LiPF₆ in EC:DMC:DME (1:1:2)</td>
<td>HOPG</td>
<td>AFM</td>
</tr>
<tr>
<td>20 [55]</td>
<td>1 M LiClO₄ in EC:DMC (1:1)</td>
<td>HOPG</td>
<td>AFM</td>
</tr>
<tr>
<td>4-5 [67]</td>
<td>1 M LiAsF₆ in EC:PC (1:1)</td>
<td>Petroleum coke particles</td>
<td>Based on irreversible capacity and specific (electrode) surface area calculations</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initial thickness: 450-980 nm After 24 cycles: 1600 nm [78]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEI Thickness:</td>
</tr>
<tr>
<td>1 M LiPF₆ in EC:DMC (1:1)</td>
</tr>
<tr>
<td>Natural graphite spheres</td>
</tr>
<tr>
<td>FIB/SEM</td>
</tr>
</tbody>
</table>

1.8. In-situ Observations of Graphite Damage and SEI Morphology

For a deeper insight into the processes at the graphite/electrolyte interface, several surface-sensitive in-situ methods were employed to observe the surface changes on cycled graphite and SEI formation. Although Raman spectroscopy is suited only for near surface studies because of the high optical extinction coefficient of carbon, it is extremely sensitive to changes that disrupt the translational symmetry of graphite planes. Therefore Raman
spectroscopy is an important tool for characterization of the electrochemical interfaces and the electrode surface features at nanometer resolution. Using confocal Raman microscopy technique, Novák et al. [74,100] conducted an in-situ investigation of SEI layer formation on graphite. Raman microscopy and AFM was used by Kostecki et al. [19] to monitor surface structural changes of MAG-10 synthetic graphite electrodes with 1 M LiPF$_6$ in EC/DEC electrolyte in lithium-ion cells cycled at room temperature and at 60°C. The increase in the intensity of the Raman D-band at 1620 cm$^{-1}$ indicated electrode surface degradation, which led to an increased anode surface reactivity with the electrolyte. The reactions led to further electrolytic decomposition and inorganic products, such as phosphates, carbonates and LiF, were found to deposit preferentially at the degraded sites. Furthermore, it was suggested that elevated temperature cycling could lead to breakdown of the graphitic structure and expose new edges and fragments that could react with the electrolyte to form inorganic compounds. In this way, accumulation of inorganic products could occur on graphite and act as a barrier to lithium-ion diffusion that subsequently reduced the cyclic performance. It was also reported that the gradual transfer of lithium from the cathode to anode and the SEI eventually prevented complete discharge of the anode that led to capacity decline.

In another study, in-situ Raman spectra were recorded from the surface of commercially available Timrex® synthetic carbon particles and presented in Fig.1.20 [74]. With decreasing electrode potential, changes in the Raman spectra were observed. The $E_{2g}(2)$ peak of the G-band, that arises due to the in-plane vibration of graphite, split into two modes that were assigned as $E_{2g}(2)$-vibrational modes of graphene sheets adjacent to a lithium layer ($E_{2g}(2b)$, displaced to a higher wavenumber), and $E_{2g}(2)$-vibrational modes of graphene sheets adjacent to other graphene sheets ($E_{2g}(2i)$). Additionally, upon formation of
Fig.1.20. In-situ Raman spectra measured at the indicated potentials from a single Timrex® synthetic graphite particle at the surface of a commercial negative electrode during the first charging at 0.1 mA/cm² in a 1 M LiClO₄ + EC/DMC electrolyte. The spectra were arbitrarily shifted on the vertical scale [74].

the lithium-intercalated graphite compound, the D-band (indicating disorder in the graphite structure) is no longer observed (Fig.1.20) possibly due to formation of an ordered structure. Markervich et al. [20] used Raman spectroscopy to estimate the decrease in graphite crystallite size as the cycling progressed. Based on the intensity of the D-band, which is inversely proportional to the crystallite size in the direction of the graphite plane [101], the size ($L_z$) of powder graphite (KS-15 from Timrex Inc.) was calculated using the following equation:
$L_a = 44 \left( \frac{I_D}{I_G} \right)^{-1}$ (1.3)

where, $I_D$ was the intensity of D-band, and $I_G$ being that of the G-band. It was seen that the average crystallite size decreased from $215 \pm 75 \text{ Å}$ in pristine electrode, to $69 \pm 34 \text{ Å}$, for cycled electrode.

Fig.1.21. The first four cyclic voltammograms at a scan rate of 5 mV/s of a fresh HOPG basal plane in 1 M LiClO$_4$ in 1:2 (by wt.) EC:PC [57].

Campana et al. [102] performed in situ AFM during CV tests to study surface changes on the basal planes of HOPG in a 1 M LiClO$_4$ in 1:2 (by wt.) EC:PC electrolyte. The CV scans obtained with a scan rate of 5.0 mV/s from 3.000 to 0.005 V vs. Li/Li$^+$ is shown in Fig.1.21. In the first cycle a small negative current peak (~10 $\mu$A/cm$^2$) at about 1.25 V was observed. Since it was only observed in the first cycle, this peak was attributed to the reduction of trace water and surface groups on the carbon surface [15]. A distinct reduction current peak with a maximum observed at about 0.75 V was attributed to the formation of
the SEI [16]. The intensity of this current peak was progressively reduced in the subsequent cycles. An onset of the reduction current at about 0.30 V was also observed. This potential corresponded to the thermodynamical potential for the lithium intercalation [103]. The cyclic voltammograms were recorded at a relatively fast potential sweep rate of 5.0 mV/s with immediate reversal of the scan direction at the lower potential limit. In high scan rate experiments, the faster surface reactions were considered as partially completed as evidenced by the decreasing intensity of the SEI formation peak with progressive cycling. During the high scan rate tests, it was assumed that the rate of lithium intercalation into the bulk of the HOPG was much slower and only a fraction of the maximum possible fully intercalated state (LiC₆) was reached. A typical AFM image, obtained during the same study, of a pristine HOPG surface at 3.000 V vs. Li/Li⁺ is shown in Fig.1.22 (a). The microstructure before the test revealed three to four steps without any observable surface features. After sweeping the potential to 0.005 V at a sweep rate of 5.0 mV/s and then holding the potential at 0.005 V for about 6 min, the SEI became visible. It can be seen in Fig.1.22 (b) that the SEI covered the entire surface. The structure of the SEI was described as globular. After 41 minutes at 0.005 V, the basal planes became distorted. Branch-like features started to develop forming a network [Fig.1.22 (c)]. The topography after 71 min of holding the potential at 0.005 V is shown in Fig.1.22 (d). The networking features became more pronounced and ran parallel as well as vertical to the edge plane. These features were elevated and have heights between 7 and 15 nm. The smaller branches were 500 nm long whereas the larger ones were as long as 4 μm. These features were explained as cycling-induced cracks on the basal graphite planes since scratching of the surface with the AFM tip did not affect these structures.
Fig. 1.22. Contact mode AFM images of HOPG in 1 M LiClO₄ (1:2) EC:PC electrolyte. The scan size was $10 \times 10 \, \mu m^2$ and the image scan rate was 1 Hz. (a) At 3.0 V vs. Li/Li⁺; $\Delta z = 10 \, nm$ (b) after 6 min at 0.005 V; $\Delta z = 25 \, nm$ (c) after 41 min at 0.005 V; $\Delta z = 15 \, nm$ (d) after 71 min at 0.005 V; $\Delta z = 15 \, nm$ [102].

SEI morphological studies using in-situ AFM techniques on the basal surface of HOPG was performed by Novák et al. [74]. During potential sweeps in EC/DMC-based electrolytes, morphology changes due to SEI formation could be detected at 0.7 V in Fig. 1.23 (a), which was shortly after ethylene gas evolution due to electrolytic reduction. It was revealed that the SEI formed initially was rough [Fig. 1.23 (b)] and does not cover the
entire electrode surface. However, after prolonged cycling, the SEI film attained a thickness of about 200 Å and covered the entire surface.

Fig.1.23. (a) In-situ AFM image showing the SEI formation in 1 M LiClO$_4$ + EC/DMC electrolyte on a step at the basal surface of a HOPG electrode. The image was recorded at one line per second during a 5.0 mV/s potential sweep from 1.3 to 0.0 V vs. Li/Li$^+$. Vertical surface profiles from (a) where (b) corresponds to a potential of 0.25 V showing 15 nm high SEI islands, and (c) shows the surface profile recorded when SEI growth was completed (at 3.0 V after 2 cycles) [74].
1.9. Surface Modification and High Temperature Treatment of Graphite Anodes for Improvement in Electrochemical Behaviour

Electrochemical performance improvement by electrode surface modification has been observed using various techniques [104-111]. For example, the morphology and chemistry of graphite surfaces were altered by mechanical milling of natural graphite particles in oxygen and nitrogen [104]. Application of carbon coatings by thermal vapor decomposition treatment at 1000°C [105] or heat-treatment of graphite/PVC mixtures at 800-1000°C in Ar [106] has also been attempted. Tin coatings were applied using autocatalytic deposition [107] and electrodeposition [108] techniques.

Shafiei and Alpas [108] electrodeposited an ultrafine grain (350±50 nm) Sn coating with a thickness of 0.5±0.1 μm on randomly oriented carbon fibres to produce an Sn-carbon fibre composite anode for rechargeable Li-ion batteries. The microstructure of the composite anode is shown in Fig.1.24 (a). An SEM image of the uniformly coated fibre’s cross-section prepared by FIB is shown in Fig.1.24 (b) revealing only a single layer of Sn grains across the thickness of the coating. Galvanostatic cycling caused disintegration of the Sn coating; the microstructure of the electrodes after 20 charge-discharge cycles can be seen in Fig.1.24 (c), while a back-scattered electron SEM image of the cross section of a carbon fibre is shown in Fig.1.24 (d). It was observed that the matrix surrounding carbon fibres were composed of fluorine and phosphorus rich compounds including Sn particles of size 1 μm to a few nanometers in diameter. A network of microcracks, observed around the fibres, were suggested to have been formed as the result of the large volume changes during the charge-discharge cycles. A higher capacity retention of 50% after twenty cycles, compared to the 23% measured for a 2.2±0.2 μm thick Sn coating deposited on a Cu foil was attributed
to the small thickness and large surface area of the Sn coating on the carbon fibres that boosted the coating’s chemical reactivity and tolerance for volume change.

Fig.1.24. SEM images of (a) the as-prepared Sn-carbon fibre electrode; (b) a cross section of a Sn-coated carbon fibre before cycling; (c) the carbon fibre electrode after 20 galvanostatic cycles; (d) a cross-section showing damage of the Sn coating [108].

Another surface modification approach for graphite anodes was developed by encapsulating polyacrylonitrile (PAN) [109] on the surface of natural graphite particles via radiation-initiated polymerization. Encapsulation of PAN contributed to the stability of the graphite particles surface during cycling. As a result, the PAN-coated graphite electrodes showed capacity improvement in PC-based electrolyte [Fig.1.25 (a)]. Graphite chemically modified by adsorption/adhesion of polydimethylsiloxane (PDMS) [110] showed a 14%
reduction in the first cycle capacity drop and also improved the cycling performance of the graphite electrode [Fig.1.25 (b)].

Fig.1.25. Comparison of cycling characteristics of natural graphite electrodes with (a) PAN encapsulated graphite electrodes at a current density of 0.2 mA/cm² in PC-based electrolyte [109], and (b) PDMS-treated graphite at C/6 rate [110].

Electrolyte modification by addition of vinyl ethylene carbonate (VEC) was suggested to promote the formation of a stable passive electrode surface that aided in an
improved cell performance [111]. In summary, application of coatings and additives was suggested to modify the electro-active locations on the graphite surfaces that could, in turn, reduce the rate of solvent molecule intercalation during SEI formation and improve cyclability.

It is important to investigate the high temperature cyclic performance of electrodes in Li-ion batteries because of their application in pure and hybrid electric vehicles, as well as for aerospace applications where they are required to operate within a broad temperature range [112-115]. Also, the microstructure, morphology and the composition of SEI formed at elevated temperatures, and their influence on electrode damage are not well understood. The change in the SEI composition at elevated temperatures has been previously investigated using diffuse reflectance (DR)-FTIR, EIS [116] and XPS [117] techniques. It is believed that the metastable components of SEI like lithium alkoxides (R-OLi) and lithium alkyl carbonates (R-OCO2Li) become unstable at temperatures typically exceeding 60°C, for LiBF4 containing electrolytes [118], and 105°C, for LiPF6 containing electrolytes [119]. These compounds may convert to the stable Li2CO3 [120]. It has been suggested that the thickness of the SEI increases at temperatures between 60-130°C [121-123]. On the surfaces of HOPG electrodes, it was observed that the thickness of the SEI layer increased from 16 nm at 30°C, to 150 nm at 80°C, in an EC-based electrolyte [124]. Increase in the irreversible charge loss at 80°C was attributed to an improved solvent decomposition and accumulation of the inorganic products on graphite particles that eventually led to capacity fading [124]. Increase in solvent decomposition could also initiate exothermic reactions leading to thermal runaway [125,126]. The electrolyte may come in contact with the graphite at temperatures ~200°C [118,127] due to decomposition of the SEI [122,127] and degradation of the electrolyte [119,122]. Degradation of electrolyte has been suggested to depend on the
magnitude of the energy stored within the cell, the cell temperature and the time duration of exposure to elevated temperatures [128]. Li-ion cells exposed to a temperature of 55°C for a short-term were shown to reduce the amount of stored electrochemical energy and improved the capability of capacity retention [128]. However, when the cells were cycled initially at room temperature and then stored at temperatures close to 80°C, the cell capacity declined promptly. The capacity fading was attributed to the repeated growth and dissolution of the SEI layer, and that a thicker SEI could provide resistance to Li-ion insertion [121,123]. Further experimental evidence is required to prove the recommended SEI degradation mechanism.

1.10. Anodes of Sn and Si Alloys for Lithium-ion Batteries

Due to graphite’s low charge capacity of 372 mAh/g, negative electrodes made of Sn and Si alloys with high capacity have also been proposed for lithium-ion batteries [129-134]. These alloys are not prone to cracking and pulverizing like bulk Sn and Si electrodes [135]. Such materials showed improved cycle life compared to their crystalline counterparts.

Optical observations of a-Si$_{0.64}$Sn$_{0.36}$ composite electrodes showing particle movement during cycling was recorded using a system shown in Fig.1.26 [136]. A fiber optic ring illuminator was added to provide illumination to the samples under the objective lens. The microscope was mounted on a steel platform suspended from springs and stretch cords in order to dampen external vibrations from affecting the microscope system. A 12 megapixel charge-couple device (CCD) single lens reflex (SLR) photographic camera (Fuji Professional) was used to record images. For in-situ AFM topographical measurements with amorphous/nano-structured alloys, a custom designed electrochemical cell was constructed [136]. Fig.1.27 shows a picture of the electrochemical ‘wet’ cell. The lithium counter and
reference (foil) electrodes were installed in the form of a ring along the interior perimeter of a ‘well’, which contained the electrolyte. Due to its excellent corrosion resistance properties, Type 430 stainless steel was used to construct the base of the cell.

Fig.1.26. In situ system for observing reaction of a-Si_{0.64}Sn_{0.36} composite electrodes with lithium [136].
Dahn et al. [137] studied the electrochemical cycling behavior of Sn-Co and Sn-Co-C prepared by sputter deposition. Despite of having an amorphous structure, Li/SnSn_{1-x}Co_x cells depicted poor cycle life due to aggregation of Sn after cycling. However, addition of carbon into the Sn_{1-x}Co_x system improved the cyclic performance that was evident from stable differential capacity vs. potential data. The improved capacity retention was attributed to the prevention of Sn aggregation by carbon during charge-discharge cycling [103]. In addition, the amorphous CoSn grains were separated by a carbon-matrix. It was suggested that alloy compositions that showed small volume expansions would be better suited for negative electrodes in commercial lithium-ion batteries.

Tian et al. [138] suggested that Si and Sn-based alloys could replace graphite as the anode material in the next generation of lithium-ion batteries. Patterned Sn_{32}Co_{38}C_{30} films
Fig. 1.28. (a) In-situ AFM images of Sn$_{32}$Co$_{38}$C$_{30}$ electrochemically reacting with lithium. (b) The potential vs. time plot, each plateau corresponding to the potentials (a-i) in the AFM results in (a) [138].

were deposited through a Ni-mesh SEM calibration grid held in firm contact with the surface of a stainless steel substrate. Volume changes of the sputtered films were measured
using in-situ AFM during electrochemical cycling against lithium. The plot for a typical potential vs. time test conducted with the deposited films is shown in Fig.1.28 (a). The AFM images of the square patches of Sn\textsubscript{32}Co\textsubscript{38}C\textsubscript{30} obtained in-situ during the voltage cycling in Fig.1.28 (a) is shown in Fig.1.28 (b). At complete lithiation, the heights of patches reached their maxima, and minima at complete de-lithiation. Additionally, there were small spikes located between the square patches that grew with the progress of charge-discharge cycles. Appearance of the spikes was attributed to the formation and accumulation of electrolyte decomposition products.

When the cell was discharged to 0.3 V, lithium began to insert into the patches that led to their expansion. When the potential was held either at 1.000 or 0.005 V (for 4 hours), the patches remained at their minimum and maximum heights, respectively. The volume of lithium atoms accommodated within the nano-composite is 8.9±0.5% cm\textsuperscript{3}/mol for SnCo, as suggested by Obrovac et al. [139]. The molar volume of lithium atoms within the carbon was assumed to be 3.4 cm\textsuperscript{3}/mol. Based on these assumptions, the theoretical estimate for the volume change was calculated as 149±6%, which was consistent with the volume change value of the Sn\textsubscript{32}Co\textsubscript{38}C\textsubscript{30} patch obtained during the experiments (147±4 %). Although the volume changes in these alloys were much higher than graphite (12%), the electrodes were durable with excellent charge-discharge capacity retention. Therefore, Sn-C and Si-C alloys could be considered as alternative anode materials for lithium-ion batteries.

1.11. Summary of Literature Survey

Significant research work related to anodic degradation mechanisms in lithium-ion batteries, and SEI film formation mechanism is present in the literature. The main conclusions of this survey are summarized as follows:
1. Graphite electrode damage has been described as exfoliation or delamination of the graphite layers. It was suggested that the graphite exfoliation was caused by the co-intercalation of solvent molecules and lithium-ions between the graphite layers during the SEI layer formation.

2. During SEI formation, carbonate solvents are reduced, forming ethylene gas and other organic and inorganic compounds. Spectroscopic results were used to understand the mechanism of SEI formation.

3. Microstructural details of anode degradation mechanisms, along with SEI film thickness, composition and morphology, reported in the literature were insufficient due to difficulties in direct observation.

The rationalization of electrode degradation mechanisms is not straightforward and current interpretations are qualitative. Lithium insertion in graphite leads to interlayer expansion but whether this is sufficient to cause exfoliation is contentious. Current Li-ion battery systems use EC-based electrolytes but then again the role of solvent decomposition products that ingress between the graphene planes are yet to be identified. These observations amplify the need for comprehensive analytical and in-situ microscopic and spectroscopic studies of damage mechanisms during the electrochemical process. In particular, the initiation and growth behaviour of cracks causing electrode fragmentation need to be determined in relationship to the SEI morphology and composition. By characterizing the micromechanisms of damage processes in graphite and correlating the microscopic information to electrochemical performance new design methods for electrode microstructures will arise leading to improvements in Li-ion battery performance.
1.12. Objectives of Research

This dissertation focuses on developing analytical characterization methods for identifying the mechanisms of surface and subsurface graphite electrode damage and SEI formation mechanisms in Li-ion batteries. The scientific methodology used was designed to achieve the following objectives:

A. Design an electrochemical cell specifically for real-time microscopy and spectroscopy observations to quantify electrode surface damage as a function of the voltage gradient, voltage scan rate, cycle time, and temperature. The implementation of an in-situ observation system during electrochemical tests using a digital optical microscope and a Raman spectrometer would help to determine the severity of surfaces degradation due to exfoliation and fragmentation of electrode particles.

B. Characterize the microstructural details of exfoliation (delamination) mechanisms at the electrode/electrolyte interfaces and electrode subsurfaces using analytical cross-sectional FIB microscopy and high-resolution TEM. Application of FIB and TEM microscopy to samples excised from cycled turbostratic graphite electrodes are expected to elucidate details of crack initiation and fragmentation process.

C. Observe the morphologies, microstructures and compositions of the SEI layers in order to understand the mechanism of SEI formation at different voltage scanning conditions and temperatures.

D. Apply surface engineering techniques to modify surfaces of carbonaceous anodes by means of aqueous deposition of Li$_2$CO$_3$ particles and electrodeposition of nanostructured tin. In this way, durable and high capacity electrodes could be developed on the basis of the microstructural investigations.
Bibliography


[38] G.E. Bacon, Crystallographic studies on graphite. United Kingdom Atomic Energy


[42] G.K. Williamson, Electron microscope studies of dislocation structures in graphite,

VonSacken, Lithium Batteries: New Materials, Developments and Perspectives (Ed. G.


[95] F. Joho, B. Rykart, A. Blome, P. Novak, H. Wilhelm, M.E. Spahr, Relation between surface properties, pore structure and first-cycle charge loss of graphite as negative electrode in lithium-ion batteries, J. Power Sources, 97-98 (2001) 78-82.


[137] J.R. Dahn, R.E. Mar, A. Abouzeid, Combinatorial study of Sn_{1-x}Co_x (0 < x < 0.6) and [Sn_{0.5}Co_{0.45}] (1-y)C_y (0 < y < 0.5) alloy negative electrode materials for Li-ion batteries, J. Electrochem. Soc. 153 (2006) 361-365.


CHAPTER 2: In-situ Observations of Lithiation/De-lithiation Induced Graphite Damage during Electrochemical Cycling

2.1. Introduction

Lithium-ion batteries have high volumetric and gravimetric energy densities exceeding 140 Wh/Kg, and a lifespan over 1000 cycles at high cell voltages (~4 V) compared to Ni-MH and other conventional battery systems. A performance limiting factor in lithium-ion batteries is that the generally used graphitic anodes suffer from severe structural damage [1-4]. It has been reported that lithiation/de-lithiation cycles, operating through the hexagonal sheets (graphene) of graphite, cause its degradation, thus, decreasing the electrode lifespan; an effect that is intensified at high charging rates and elevated temperatures [5-7]. It has been suggested that lithium-ions diffuse into the graphene layers through the edge planes [8]. Introduction of localized stresses generated during electrochemical cycling leading to breaking of C-C bonds, as determined by Raman spectra [9], was thought to cause surface structural disordering. Also, quantitative Raman mapping of anodes was achieved using intensity ratio of disordered (D-band) to ordered (G-band) graphite peaks. For example, $I_D/I_G = 0$ for a perfect graphene layer increased to 0.60 after shallow cycling, and to 0.45 after deep cycling; this indicated that the maximum damage was inflicted to the graphite surface during initial stage of lithium intercalation into graphite [9]. Raman spectroscopy was used as an in-situ damage monitoring technique by Novak et al. [10] for carbon particles on the surface of negative electrodes. With decreasing electrode potential, changes in the Raman spectra were observed. Upon formation of lithium-intercalated graphite compounds, the D-band was no longer observed.
An important aspect of cycling of a lithium-ion battery is the oxidation of lithium at the negative electrode and formation of a solid electrolyte film (SEI). The intercalant species react with the solvent species producing SEI and cause irreversible loss of lithium accompanied by loss in coulombic capacity [11]. Morphology changes due to SEI formation were detected by in-situ AFM technique [10] revealing that the SEI, with high surface roughness, does not cover the electrode surface initially but eventually attain a thickness of 200 Å, covering the entire surface. It has been suggested that graphite exfoliation was ultimately stopped by the formation of this protective film [12]. Christensen and Newman’s mathematical model [13] predicted that in carbonaceous materials, undergoing volume expansion during lithium insertion, the particle surface is most likely to fracture at the end of extraction. Deshpande et al. [14] developed theoretical model for diffusion-induced stress in electrodes and concluded that the driving force and probability of cracking during de-lithiation and lithiation are different. Ohzuku et al. [15] and Sawai et al. [16] used acoustic emission technique on electrolytic MnO₂ particles used as anode and concluded that an accelerated rate of fracture occurred during the first discharge, followed by almost negligible damage during charging. Harris et al. [17] performed in-situ optical microscopy at low magnification (90×) and the electrochemical data was mathematically modeled to predict lithium diffusion rate in graphite electrodes. The model, constructed on the basis of color changes in graphite, induced by variations in lithium-ion concentration, required microstructural information for further quantification.

In this work, details of degradation of graphite surfaces during electrochemical cycling were observed by in-situ optical microscopy operated at 1000× magnification. Degradation events by loss of electrode particles were observed sequentially during lithiation and de-lithiation stages. Graphite electrodes were cycled starting from the peak as well as the
base voltage to elucidate the role of passivating film formation (SEI) on graphite electrode damage. The role of peak voltage values and scan rates were also studied.

2.2. Experimental

A 99.999% pure graphite (obtained from Kurt J. Lesker Company, Canada, containing traces of Al, Fe, Mg and Si, with specific gravity ranging between 1.8 - 2.1) electrode of 5 mm diameter was placed at the center of the electrochemical cell constructed using PTFE. A quartz glass optical window was installed in the cell cover for the graphite surface observation. The cell was assembled and sealed in an Ar-filled glove box. The top surface of the graphite was observed using an optical microscope with large depth of field. The graphite was cleaned ultrasonically using acetone to remove the loose carbonaceous particles from the natural pits present. A 99.99% pure lithium wire with a resistivity of 9.446 $\mu\Omega$-cm (at 20°C) was used as counter electrode. The reference electrode was also made of a pure lithium wire. The electrolyte solution was formed using 1 M LiClO$_4$ in a 1:1 (by vol.) mixture of ethylene carbonate (EC) and 1,2-dimethoxy ethane (DME). Electrochemical experiments consisted of cyclic voltammetry tests performed using a Potentiostat/Galvanostat operated between 0 and 1.000/3.000 V at different scan rates of 2.00 mV/s and 500 $\mu$V/s. The open-circuit potential (OCP) of the completed lithium-ion cell was 3.200 V, measured using a digital voltmeter (measuring DC voltage data with ± 0.025% accuracy).

2.3. Results

Electrochemical cycling experiments were performed such that graphite electrodes were subjected to de-lithiation and lithiation stages separately:
To study graphite damage during the de-lithiation stage, the voltage was gradually increased from the base value of 0.000 V to 3.000 V at a linear scan rate of 2.00 mV/s [Fig.2.1 (a)] and optical images were recorded simultaneously at particular instances [Figs.2.1 (b) - (e)] indicated in the inset. The appearance of dark colored spots seen in the sequence of the optical microscope images in Figs.2.1 (b) - (e) indicates loss of material from graphite surface and formation of pits during the de-lithiation of the electrode. The area fraction of the damaged regions increased with the voltage and also there was an increase in the size of the existing spots. The rapidly increasing number and size of the pits was observed to occur until the potential increased to 0.134 V [Fig.2.1 (d)]. Almost all damage on graphite surface occurred within a short time period (< 100 s) after the start of the experiment. Graphite damage continued until the potential difference, $\Delta V$, between the OCP (3.200 V) and the operating voltage (0.134 V) reached 3.060 V, after which almost no new pit formation was observed [Fig.2.1 (e)], and stopped completely when the voltage reached its peak value (3.000 V).

When a lower voltage scan rate of 500 $\mu$V/s was used [Fig.2.1 (f)], the extent of pit formation was more conspicuous and the damage rate was faster [as shown in Figs.2.1 (g) - (j)] compared to that observed at 2.00 mV/s. More specifically, for a given $\Delta V$, more damage was inflicted when a low scan rate was used; this could be seen by noting the higher graphite pit area fraction at 0.017 V (for $\Delta V = 3.183$ V at 500 $\mu$V/s) shown in Fig.2.1 (i), compared to that at 0.015 V (for $\Delta V = 3.185$ V at 2 mV/s) shown in Fig.2.1 (c).
Fig. 2.1. De-lithiation step in a cyclic voltammetry experiment, indicating variations in voltage and current density with time, performed between (a) 0.000 and 3.000 V at a linearly increasing scan rate of 2.00 mV/s with in-situ digital microscope images at 1000× showing the (b) initial condition, and after (c) 9 s, (d) 70 s, and (e) 820 s. Typical damage features are marked in Figs. 2.1(b) - (e).

The initial high slope of the current density curves in Fig. 2.1 (a) and (f) could be attributed to the presence of lithium ions that were already diffused inside the graphite from the electrolytic solution containing LiClO₄ (in a polar solvent), before the start of the experiment. Simultaneously, a severe drop was registered in the resistance of the working electrode.
Fig. 2.1. (contd.) De-lithiation experiment performed between (f) 0.000 and 1.000 V at a linearly increasing scan rate of 500 μV/s with in-situ digital microscopy images at 1000× showing the (g) initial condition and after (h) 6 s, (i) 45 s, and (j) 90 s. Typical damage features are marked in Figs. 2.1(g) - (j).

Damage during the lithiation stage of graphite was studied starting from the peak potential (1.000 V) and by decreasing the potential to 0.000 V using a scan rate of 500 μV/s, as shown Fig. 2.2 (a). The recorded images [Figs. 2.2 (b)-(c)] indicate that, during lithiation the surface damage was almost negligibly small. The size and area fraction of the surface pits increased at a much slower rate than those observed at de-lithiation stage. A careful inspection of the surface images reveals a slight overall contrast change on the graphite
surface for which the initial lighter tone darkens slowly as the potential decreased as shown in Figs. 2.2 (b) to (c).

Fig. 2.2. Lithiation step in a cyclic voltammetry experiment, indicating variations in voltage and current density with time, performed between (a) 1.000 and 0.000 V at a linearly increasing scan rate of 500 μV/s with in-situ digital microscopy images at 1000× showing the (b) initial condition, and after (c) 380 s, (d) 900 s, and (e) 1380 s. Typical damage features are marked in Figs. 2.2(b) - (e).

The development of this darker contrast is an indication of formation of a surface film due to electrolytic reduction. It was noted that the electrode current density decreased [Fig. 2.2 (a)] during lithiation. The decrease was attributed to an irreversible consumption of
lithium ions, initially present at the graphite electrode/electrolyte interface during the formation of the surface film.

![Cyclic voltammetry plot](image)

**Fig.2.3.** (a) Cyclic voltammetry plot when high purity graphite electrode undergoes a complete cycle between 3.000 and 0.000 V at 2.00 mV/s scan rate. 3-dimensional digital microscope images show graphite surface at (b) initial condition (at 3.000 V), and changes after (c) 1200 s and (d) 1600 s.

Fig.2.3 (a) shows a complete lithiation/de-lithiation cycle experiment, which was initiated from the lithiation step at 3.000 V (at 2.00 mV/s). Three critical instances of the lithiation stage [Figs.2.3 (b) - (d)] are indicated by the 3-dimensional optical images recorded during the experiments. Darkening of the graphite surface due to layer formation is clearly observed when images corresponding to the initial surface condition [Fig.2.3 (b)] and that
recorded at 0.604 V [Fig.2.3 (c)] are compared. Yet, surface pitting damage was almost insignificant. As the voltage decreased from the peak value, large scale fluctuations in the resistance curve [Fig.2.3 (a)] were observed, which indicated occurrence of electrochemical reactions at the graphite/electrolyte interface and formation of a surface layer. The resistance curve eventually stabilized at a low value (~1.54 Ω). Some graphite surface damage occurred at the subsequent step [Fig.2.3 (d)] but the amount of damage was minute. The loss of graphite particles from the surface was first observed when the voltage decreased to ~0.500 V (corresponding to ΔV = 2.700 V at 1,250 s), and continued until the base voltage (0.000 V) was reached.

2.4. Discussion

The sequence of the damage events occurring during electrochemical cycling of graphite could be summarized schematically as in Fig.2.4. For the experiments starting from the de-lithiation step, graphite particle removal occurred immediately (see Stage A in Fig.4) and continued until a critical voltage (V_{crit}) was exceeded. The potential difference, ΔV, defined as the difference between the OCP, and the operating voltage, V, acted as the driving force for graphite surface damage, which continued until, ΔV ≥ ΔV_{crit} (where, ΔV_{crit} = OCP - V_{crit}). The linear voltage scanning rate used was important in controlling the magnitude of damage. At low scan rates, longer times were required for ΔV to decrease to ΔV_{crit}. Thus, the graphite electrode was subjected to damage for a longer duration, compared to the experiments operating at high scan rates where less graphite damage occurred as depicted in Fig.2.1. As the cycle shifted to the lithiation step (Stage B in Fig. 2.4), no further damage was observed as the electrode surface became passivated as a result a formation of a
film. In the subsequent cycles as the surface film protected the graphite electrode from further deterioration.

Fig. 2.4. Schematic illustration of the damage related events in graphite when cycle starts with (a) de-lithiation (when extensive loss of graphite particles constituted damage) and (b) lithiation (when surface film formation prevented graphite damage).

When the experiments started from the peak voltage (Stage C in Fig. 2.4), damage was delayed until $\Delta V$ exceeded a critical value, $\Delta V_{\text{crit}}$, and continued until the base voltage (0.000 V) was reached. But, unlike the events occurring during the de-lithiation stage, the process of a protective surface film formation preceded the damage events in this case. Thus, the magnitude of damage in this case was far less than that occurring during the de-lithiation stage. The gradually increasing $\Delta V$ (beyond the $\Delta V_{\text{crit}}$) still left the graphite surface
prone to damage. As the film thickness increased (e.g. Stage D in Fig. 2.4), graphite damage was arrested. Therefore, the experimental results infer that a pre-existing surface film would prevent initial graphite damage and the presence of a stable film would improve the durability of graphite electrodes.

2.5. Conclusions

The main conclusions of this study can be summarized as follows:

1. Extensive loss of graphite particles from the working electrode surface was observed when voltammetry experiments initiated from the de-lithiation stage. The surface film, which formed during the lithiation stage prior to the initiation of damage, reduced the intensity of graphite degradation.

2. Potential difference exerted on the working electrode acted as the driving force for graphite surface damage. Damage in graphite was arrested during de-lithiation, and initiated during lithiation stage, only when the operating voltage reached a critical value; the magnitude of damage in lithiation stage was much less than that occurring during de-lithiation.

3. The voltage scan rate was an important factor in controlling the damage during de-lithiation. At high scan rates graphite damage was less severe as the operating voltage increased rapidly to reach a critical value.

Bibliography


CHAPTER 3: A Transmission Electron Microscopy Study of Crack Formation and Propagation in Electrochemically Cycled Graphite Electrode in Lithium-ion Cells

3.1. Introduction

Understanding lithium intercalation processes that occur in graphite negative electrodes is of considerable importance for enhancing the performance of rechargeable lithium-ion batteries [1-6]. Graphite is the preferred anode material as it offers high voltages of 3 - 4 V when used against commercial cathodes, e.g. LiCoO₂, LiMn₂O₄, or LiFePO₄. Graphite has high lithium storage capacity (theoretically each Li atom co-ordinates with six C atoms). The volume change of graphite during the intercalation/de-intercalation process is typically in the order of 12% and hence not severe. Yet, graphite electrodes exhibit a drastic capacity drop, especially during the initial stages of the electrochemical process. The capacity drop is accompanied by surface damage, generally described as graphite exfoliation, or removal of graphite layers near the surface [7-11] and also as the detachment of graphite from the surface in the form of particulates [8,11].

Experimental studies were conducted to estimate the damage caused by lithium-ion intercalation/de-intercalation induced stresses within a graphite lattice using techniques such as Raman spectroscopy and atomic force microscopy [12,13]; these stresses were thought to cause ‘surface structural disordering’ by deformation of the graphene layers and breaking of the C-C bonds. The use of ex-situ Raman spectroscopy [14] provided evidence for fracture and fragmentation of graphite particles during electrochemical cycling and a decrease of the average size of graphite (plate-like, \( a \gg r \)) crystallites. On the other hand it was suggested that the process of lithium insertion in graphite is highly dependent on the electrolyte.
composition, which also determines the electro-mechanical stability of graphite electrodes in lithium salt solutions during electrolytic decomposition [15]. The decomposition products are known to form a solid electrolyte (SEI) layer that cover the electrode’s surface [16,17]. Investigations made using focused ion beam (FIB) microscopy revealed some details of the formation of the SEI layer on natural graphite spheres during galvanostatic charge/discharge tests [18]. Accordingly, the initial thickness of SEI under these testing condition was found to vary between 0.5 - 1.0 μm and had a rough, non-uniform morphology, but eventually attained a uniform thickness of approximately 1.6 μm after 24 cycles. Aurbach et al. [19] suggested a capacity-fading mechanism due to exfoliation of the graphite particles by co-intercalation of solvent molecules together with Li+. Results of investigations conducted using a broad range of surface sensitive analytical tools, including XPS, XRD, FTIR, X-ray, and EIS [8,20,21], revealed that degradation of graphite surfaces was facilitated when the solvent molecules present in the electrolyte become intercalated into the graphite layers adjacent to the surfaces. These studies also suggested that diffusion of electrolyte solution inside the graphite cracks would accelerate anode degradation. Similarly, gas evolution during electrolytic reduction was proposed to cause the degradation [18]. Using in-situ AFM technique, Tian et al. [22] observed volume changes as high as 204% in nano-structured Sn_{1-x}Co_{x}C_{y} thin films during each charge/discharge cycle of galvanostatic tests. Harris et al. [23] performed in-situ optical microscopy (90×) and by observing colour changes in graphite electrodes, induced by variations in lithium-ion concentration, predicted the diffusion rate of lithium in electrodes. Using high magnification (1000×) in-situ optical microscopy, Bhattacharya et al. [24] observed the sequence of graphite surface damage events during de-lithiation, and suggested that the potential difference exerted on graphite electrode acted as the driving force for damage. It was also observed that a surface film, which formed during
the lithiation stage prior to the initiation of damage, reduced the intensity of graphite degradation.

The TEM investigations shed light on the structure and composition of lithium intercalated graphite compounds and lithium distribution in the graphite lattice [25-27]. Sato et al. [28] used high resolution (HR)-TEM to investigate the difference in the microstructure between a lithium charged poly(p-phenylene) (PPP)-based (disordered or non-graphitic) carbon (LiC₆), formed by electrochemical cycling against lithium, and the pristine PPP-based carbon. By analyzing the fast Fourier transform (FFT) patterns, the interplanar spacing of graphite was estimated to increase by nearly 10% to 0.40 nm following lithium insertion in disordered carbon. Song et al. [26] lithiated graphite electrodes by physical contact (short circuit) with lithium foil, and studied the distribution of lithium-carbon phases using dark-field TEM imaging with SAED patterns. It was suggested that the phases can co-exist; LiC₁₂ being mainly located closer to the surface, and LiC₆ was the principal phase in the bulk. Therefore, continuation of analytical HR-TEM studies are needed to better establish details of the subsurface defect structure of cycled graphite electrodes in order to understand the micromechanisms of graphite damage at the SEI/graphite interface.

Accordingly, the objective of this research was to observe subsurface defects and the local compositional changes that occurred in anodes made of graphite and subjected to cyclic voltammetry tests. These tests were well suited to study the effect of applied voltage on graphite damage. Cross-sectional FIB-milled microstructures were used to observe the morphologies of graphite cracks formed during the cycling, as well as the deposition of SEI layers on the graphite anode surface and inside subsurface cracks.
3.2. Materials and Methods

3.2.1. Description of Electrochemical Tests

Electrochemical experiments were performed using a specially designed test cell. A schematic of the experimental set-up is shown in Fig.3.1, with the actual image of the electrochemical cell presented in the inset. A negative electrode made of 99.999% purity graphite (Kurt J. Lesker, Canada) with density of 1.95±0.21 g cm\(^{-3}\) and containing traces (~10 ppm) of Al, Fe, Mg and Si was used.

![Experimental set-up for in-situ observation of graphite surface damage in a lithium-ion cell using an optical microscope.](image)

The graphite was micro-wire EDM machined in the shape of a cylindrical electrode with a diameter of 5 mm, and a height of 4.5 mm. The electrode was placed at the center of the electrochemical cell, which was assembled and sealed in an Ar-filled MBraun LABstar workstation with H\(_2\)O and O\(_2\) levels maintained below 1 ppm. The electrochemical cell was
constructed from polytetrafluoroethylene (PTFE), and had a quartz (optical) glass window on its top surface for graphite surface observation by an optical microscope during the test. A 99.99% pure lithium wire with a resistivity of 9.446 μΩ cm (at 20°C) was used as the counter electrode. The reference electrode was also made of a pure lithium wire. The electrolyte solution consisted of 1 M LiClO₄ (99%, Alfa Aesar®) in a 1:1 (by vol.) mixture of ethylene carbonate (EC, 99%, Alfa Aesar®) and 1,2-dimethoxy ethane (DME, 99+%, stabilized with 0.01% BHT, Alfa Aesar®). The surface areas of the counter and reference lithium wires were 296 mm² and 95 mm², respectively. Prior to placing inside the cell, the surface of graphite was cleaned ultrasonically using acetone. Using Teflon, the lateral surfaces of the graphite was covered, leaving only the top surface (having an area of 19.6 mm²) to be exposed to the electrolyte. Electrochemical tests were performed using a Potentiostat/Galvanostat (Solartron Modulab System) having a high-speed data acquisition rate (up to 1 MS/s).

3.2.2. Surface Changes due to Electrochemical Cycling

An optical microscope with a large depth-of-field was placed directly above the glass window of the electrochemical cell and the surface of graphite was observed at 1000× magnification during the electrochemical tests providing in-situ images of the surface damage events. Cyclic voltammetry (CV) tests were conducted between 0.0 and 3.0 V (vs. Li/Li⁺) using five different scan rates between 50 μVs⁻¹ and 5 mVs⁻¹. CV test data obtained from the first cycle of constant scan rate tests that were conducted at 50 μVs⁻¹, 100 μVs⁻¹ and 2 mVs⁻¹ (Fig.3.2) show that the peak current density increased with the scan rate as expected.
Fig.3.2. Cyclic voltammetry plots for graphite electrodes showing the first cycles performed between 0.0 and 3.0 V using scan rates of 50 $\mu$Vs$^{-1}$, 100 $\mu$Vs$^{-1}$ and 2 mVs$^{-1}$.

The graphite electrode surface was examined prior to the tests and as shown in the SEM image in Fig.3.3 (a), exhibited defects in the form of cavities with a diameter of 13.00±4.24 $\mu$m. SEM examination of graphite electrode surfaces after the electrochemical tests [Fig.3.3 (b)] revealed that the area fraction of cavities increased considerably. The pre-existing cavities acted as growth sites for the ones formed during electrochemical cycling. In addition to an increase in their number, the size of the cavities became larger during the CV tests. For example, only after the first cycle, the tests conducted at 2 mVs$^{-1}$ produced cavities
of 17.50±17.67 μm in diameter and 27.50±3.53 μm in depth on the graphite surface [Fig.3.3 (b)] due to loss of graphite from these locations.

![Fig.3.3. SE-SEM images of graphite surfaces (a) before cycling showing the presence of natural cavities, and (b) after cycling between 0.0 and 3.0 V at a linear scan rate of 2 mVs\(^{-1}\), revealing sites of cavities due to graphite particle removal (exfoliation).](image)

Using quantitative metallography, the area percentage of the damaged regions formed on the cycled graphite surface was calculated and plotted in Fig.3.4. It was observed that at low scan rates, e.g. at 500 μVs\(^{-1}\), the area percent increased abruptly to 30% within the first 25 s. For a high scan rate of 10 mVs\(^{-1}\), only 15% of the area was removed within the same time period. Thus, the majority of damage occurred during the initial stage of the experiment, and its severity increased when a low voltage scan rate was used. For tests performed between the scan rates of 2-10 mVs\(^{-1}\), the percentage of graphite particle removed was 20% at the end of 200 s. After this initial stage the extent of surface damage occurred was at much slower rate regardless of the scan rate.
Fig. 3.4. Plot showing calculated area percent of cavities formed on graphite surface at different voltage scan rates. The area percentage of the surface cavities were monitored for the initial 200 s of each experiment. The arrows show no further change in area percentage until the end of the test (1000 s).

3.2.3. Preparation of Cross-sectional TEM Samples using FIB in situ Lift-out Technique

At the end of each test, graphite electrodes were washed in the electrolytic solution and prepared for microscopical investigations. Cross-sectional samples were excised using focused ion beam (FIB) milling technique from the locations where graphite surface damage was observed in the form of cavities. A Zeiss NVISION 40 dual beam SEM/FIB was used to investigate subsurface damage features generated in the interior of these cavities on the sections taken perpendicular to the graphite electrode surface.
Fig. 3.5. SEM images illustrating the preparation steps of TEM sample by FIB “lift-out” method from a graphite electrode cycled between 0.0 and 3.0 V at a linear scan rate of 5 mVs$^{-1}$ for 50 cycles: (a) Two trenches are ion-milled at a specific location across the graphite surface to produce a thin lamella. (b) A micro-manipulator is positioned at the top of the region of interest in the lamella. (c) The tip of the micro-manipulator was welded to the membrane using a thin layer of carbon. (d) The sample is lifted out of the trench.

Care was taken to avoid potential ion-beam induced surface damage during FIB milling by depositing a 1 μm thick layer of carbon across the area where the cross-sectional cut was made. A trench was milled normal to the deposited carbon layer, using Ga$^+$ ions sputtered at an accelerating voltage of 30 kV, and a beam current of 80 pA. The final milling of the cross-sectional sample was conducted at a low ion-beam current of 40 pA to minimize the prospect of beam damage on the section prepared.
TEM samples were prepared using the FIB in-situ “lift-out” technique. The main steps of the lift-out TEM sample preparation technique are shown in Figs.3.5 (a)-(d) and details are described in the figure captions. Briefly, a thin platelet of ~ 2 \( \mu \text{m} \) thickness was formed on graphite surface by ion-milling trenches on either sides of it [Fig.3.5 (a)]. A micro-manipulator with a tungsten-tip was placed at the top of the sample [Fig.3.5 (b)]. The edges of the sample were then milled completely as shown in Fig.3.5 (c). The platelet, disconnected from rest of the graphite, was lifted out [Fig.3.5 (d)] and fixed to a Cu-grid (TEM sample holder). The sample was further milled to a final thickness of approximately 100 nm and then transferred to the TEM. A JEOL 2010F STEM was used to observe the cross-sectional microstructures at an operating voltage of 200 kV. A FEI Titan 80-300 TEM equipped with a hexapole-based aberration corrector for the image-forming lens, having a lateral resolution < 1 Å and operated at 300 kV, was used for high-resolution imaging of graphite layers.

3.3. Results and Discussions

3.3.1. Observation of Subsurface Damage in Cycled Graphite Electrodes

Fig.6 shows a cross-sectional SEM image of the subsurface region of a graphite electrode cycled at a scan rate of 5 mVs\(^{-1}\). This section was taken from the area marked in Fig.3.5 (a), where formation of interlayer cracks in graphite adjacent to the interface between graphite and SEI can be seen. The linear density of the cracks along the interface was measured as 2.83\( \times \)10\(^{-3}\) nm\(^{-1}\). These cracks extend parallel to each other and appeared to have caused partial delamination of graphite layers at the SEI/graphite interface at the locations indicated in Fig.3.6. The morphology of the SEI layer formed at the interface can also be seen in the same figure. The SEI layer consisted of submicroscopic particles that were agglomerated and adhered to graphite surface.
Fig. 3.6. Cross-sectional SEM image of the subsurface region (marked in Fig. 3.5 (a)) of the graphite electrode cycled between 0.0 and 3.0 V at a linear scan rate of 5 mVs⁻¹, showing the presence of cracks resulting in partial delamination of graphite layers at the SEI/graphite interface.

A bright-field TEM image of the same section shown in Fig. 3.6 is given in Fig. 3.7 (a) where the boundary (interface) between graphite and the SEI is marked. Many graphite cracks propagated obliquely to the SEI/graphite interface for 2-3 µm. The cracks were partially separated and the crack faces were connected by a few strands or layers of graphite. These graphite layers, or fibres, indicated in Fig. 3.7 (a) by arrows, appear to bridge the crack faces. Thus, the graphite crack growth process can be said to exhibit a quasi-ductile debonding behaviour rather than a cleavage-type brittle fracture [29] typically observed at the basal planes of graphite. Several typical damage features of interest are marked on Fig. 3.7 (a) and examined in more detail.
Fig. 3.7. (a) A low magnification, bright-field TEM image of the same region shown in Fig. 3.6, at the SEI/graphite interface. (b) High-magnification bright-field TEM image obtained from a region, marked as (b) in (a), revealing a granular appearance of the electrode/electrolyte interface. SAED patterns obtained from (c) a region [marked as (c) in (a)] in bulk graphite, and (d) from a region [marked as (d) in (a)] in the SEI layers.
Fig. 3.7 (b) is a high-magnification bright-field TEM image, obtained from the area marked as (b) in Fig. 3.7 (a), revealing the microstructure of electrode/electrolyte interface, where the cracks in graphite at this location were formed in the \{100\} direction (determined by the orientation of $g_{100}$ vector) and approximately at 45-60° with respect to the interface. The interface between the graphite and the SEI layer consisted of nanocrystalline grains of diameter 50-200 nm. SEI was found to deposit inside the crack. Fig. 3.7 (c) is a selected area electron diffraction (SAED) pattern obtained from an undamaged region within graphite (marked as (c) in Fig. 3.7 (a)) few microns away from the interface. Diffraction spots were obtained from different crystallographic planes of graphite with the highest intensity received from \{002\} family of planes having a $d$-spacing of 0.34 nm [30]. In addition, diffraction spots were obtained from \{004\} ($d$-spacing = 0.17 nm) and \{100\} ($d$-spacing = 0.20 nm) family of planes, again typical of pristine graphite planes. The diffraction conditions of the SEI and damaged graphite were also analyzed. A SAED pattern obtained from a region in the SEI layers (marked as (d) in Fig. 3.7 (a)) is presented in Fig. 3.7 (d). Analyses of the rings of diffraction spots revealed presence of crystallographic planes with $d$-spacings of 0.42 nm and 0.28 nm, which correspond to the \{110\} and \{002\} planes of Li$_2$CO$_3$ [31]. Diffraction ring patterns corresponding to a $d$-spacing of 0.25 nm were also identified in SEI, which could either be interpreted as corresponding to the \{101\} planes of Li$_2$O$_2$ [32] or to the \{020\} planes of Li$_2$CO$_3$. It is believed that the nanocrystalline grains observed at the interface contained these lithium compounds. The identification of \{002\} planes in Li$_2$CO$_3$ compound formed at the SEI/graphite interface is noteworthy as it was pointed out that lithium-ion diffusion would take place primarily through the (002) plane in Li$_2$CO$_3$ [33].
3.3.2. Characterization of Subsurface Cracks in Graphite

A TEM image showing the tips of a group of fine cracks formed within the graphite in a region approximately 250-300 nm away from the SEI/graphite interface (marked as AA' in Fig.3.7 (a)) is given in Fig.3.8 (a).

Fig.3.8. (a) Bright field TEM image of electrochemically cycled graphite from a region close to the interface [marked as AA' in Fig.3.7 (a)] revealing graphite layer delamination initiated with the formation of crack tips. (b) HR-TEM image of the region, indicated as (b) in (a), revealed the point of separation of two graphite layers (consisting of graphene planes) and depicted the root of a crack. A tilt was observed between the crack faces, which consisted of the (002) planes of graphite. (c) Reduced FFT-derived diffraction patterns confirming the presence of Li-C compounds only at the root of layer separation as seen in (a).
The crack faces maintained an almost parallel orientation with a crack opening displacement of \(18 \pm 5.7\) nm. According to the HR-TEM image in Fig.3.8 (b) showing the structure of graphene planes near the crack tip, (002) planes of graphite at each face of the crack formed a tilt angle of \(12.3 \pm 0.25^\circ\), at a distance less than 100 nm from the crack tip. A reduced fast Fourier transform (FFT) derived diffraction pattern [Fig.3.8 (c)], obtained from the graphite layers at the tip of the crack, specifically from the region (e) in Fig.8 (b) identified the presence of lithium compounds. The lithium compounds identified near the crack tip included LiC\(_6\), which was discerned by means of reflections from the \{001\} planes with a corresponding \(d\)-spacing of 0.37 nm [34]. Other compounds detected within the graphite lattice included Li\(_2\)CO\(_3\) according to the reflections from the \{110\} planes with a \(d\)-spacing of 0.42 nm, and Li\(_2\)O according to the reflection from the \{111\} planes with a \(d\)-spacing of 0.27 nm. These observations serve to provide crystallographic evidence that lithium intercalation could be accompanied by solvent co-intercalation.

3.3.3. Mechanisms of Crack Formation and Propagation during Lithiation/De-lithiation

A well-developed crack is shown in the high magnification bright field TEM image in Fig.3.9. The crack shown in Fig.3.9 is typical of many cracks of similar size observed in graphite and serves to illustrate some important aspects of crack growth mechanisms in electrochemically cycled graphite electrodes using voltage scan rates from 500 \(\mu\)Vs\(^{-1}\) to 5 mVs\(^{-1}\) between 0.0 and 3.0 V. It is noted that very thin translucent but continuous layers of approximately 25 - 50 nm in thickness were formed at the crack tip and along the crack faces. These layers are believed to consist of lithium compounds (e.g., LiC\(_6\), Li\(_2\)CO\(_3\), and Li\(_2\)O) similar to those identified for the crack in Fig.3.8.
Fig. 3.9. A high magnification BF-TEM image revealing the deposition of SEI layers at the crack tip, and a typical example of a delaminated graphite layer marked as B in Fig. 3.7 (a) extending across the crack faces.

The formation of these compounds indicate that solvent co-intercalation at the crack tip may play an important role in delaying graphite crack growth. Considering that graphite undergoes cyclic crack opening and closure processes under the stresses induced during lithiation and de-lithiation cycles [35-37], a fracture mechanics argument can be made to describe the graphite crack extension rate of a crack with length \(a\) per electrochemical cycle, \((da/dN)\), where \(dN\) consists of a complete voltage cycle (0.0 ↔ 3.0 V):

\[
\frac{da}{dN} = C \Delta K^m
\]  

(3.1)

where \(\Delta K (= K_{max} - K_{min})\) is the cyclic stress intensity factor. In the presence of SEI deposits at the crack tip, crack flanks make physical contact at a high positive stress intensity value, \(K_r > K_{min}\), in a way akin to the phenomenon known as roughness or asperity induced \((K_r)\) crack closure [38]. Hence, the formation of the SEI deposits at the crack tip will cause crack flanks
to reduce the effective $\Delta K$ value and, therefore, the graphite crack growth rate will be reduced proportional to the thickness of SEI. Further cyclic voltammetry tests with controlled $\Delta K$ values applied during lithiation and de-lithiation cycles will help to determine the graphite crack propagation rates. Once the growth behaviour of cracks that appear to be nucleated mostly during the first cycle is determined, the associated capacity loss due to graphite electrode degradation could be better understood.

Another mechanism that contributes to the reduction of graphite crack growth rate is attributed to bridging of faces of the crack by graphite layers or fibres. A representative example of graphite fibres connecting the two flanks of a crack is shown in Fig.3.9. These fibres help to keep the graphite crack faces bridged together, thus increasing the stress intensity level needed to cause further growth.

![Crack bridging by formation of interconnected graphite fibres](image)

**Fig.3.10.** A schematic showing the occurrence of mechanisms responsible for possible reduction in graphite crack growth; deposition of the co-intercalation compounds near the crack tip causing partial closure of crack, and crack face bridging by graphite fibres.

In summary, the TEM observations on the propagating graphite cracks during electrochemical cycling at constant voltage scan rates identified two mechanisms, namely, crack closure and crack face bridging. These two mechanisms are shown schematically in
Fig. 3.10, each contributing to the decrease of crack tip stress intensity and possibly playing a role in electrochemical cycling-induced degradation and loss of capacity of graphite electrodes.

3.4. Conclusions

Cyclic voltammetry tests were performed on graphite working electrodes to study the effect of the applied voltage on graphite damage. Graphite was cycled between 0.0 and 3.0 V vs. Li/Li⁺ in an electrolyte composed of 1 M LiClO₄ in a 1:1 volumetric mixture of ethylene carbonate (EC) and 1,2-dimethoxy ethane (DME). FIB-milled cross-sectional microstructures taken from the cycled graphite samples were used to observe the morphologies of graphite cracks formed during cycling. The microstructural observations revealed some key mechanisms that control the formation and the propagation of cracks in graphite electrodes. The main conclusions are as follows:

1. Cross-sectional subsurface structure of cycled graphite revealed partial delamination of graphite layers at the SEI/graphite interface. Nanocrystalline grains observed within the SEI layer at the interface revealed the presence of Li₂CO₃.

2. Small cracks with tip angle of 12.3° were observed between the {002} planes of graphite about 250-300 nm away from the SEI/graphite interface. FFT-derived diffraction patterns revealed the presence of lithium compounds, LiC₆, Li₂CO₃ and Li₂O, incorporated in the graphite lattice preferentially at the root of graphite cracks.

3. Deposition of SEI layers at the crack tip possibly reduced the effective cyclic stress intensity factor, thereby decreasing crack growth rate. A crack bridging mechanism through the graphite fibres that interconnected the crack faces also provided resistance to crack propagation.
Bibliography


CHAPTER 4: Micromechanisms of Solid Electrolyte Interphase Formation on Electrochemically Cycled Graphite Electrodes in Lithium-ion Cells

4.1. Introduction

The electrolyte used in a lithium-ion battery usually consists of a molar solution of a lithium salt, namely LiClO₄, LiPF₆ or LiAsF₆, dissolved in a volumetric mixture of ethylene carbonate (EC) and 1,2-dimethoxyethane. This electrolyte is known to undergo electrochemical decomposition at the graphite anode surface during electrochemical cycling. It is commonly observed that electrolyte decomposition products form a layer on the anode surface known as the solid electrolyte interphase (SEI) [1]. The SEI is a passive layer that is considered to block electron transport while allowing Li⁺ to diffuse through during cycling [2], provided that it remains mechanically stable and maintains good adhesion with the anode surface [3]. Characterization of the properties of this SEI layer is important in order to better understand the electrochemical decomposition processes and for ensuring the good cyclability of lithium-ion batteries. For these reasons the structures, chemical compositions and morphologies of these SEI layers have been the subjects of several investigations.

The early work of Peled et al. [1], based on A.C. measurements, suggested that the SEI layer might have a microstructure consisting of a mixture of several phases [4] with inorganic compounds such as Li₂O and LiF dominating the inner part close to the graphite, and semicarbonates, polyolefins, etc. forming in the outer part. Other experimental work based on differential electrochemical mass spectrometry (DEMS) has indicated that the SEI formation mechanism might involve the co-intercalation of Li⁺ [5] along with the reduction of EC at the graphite electrode surface. The reduction of EC is typically assumed to occur
during the first cycle within the voltage range of 0.3 and 0.8 V [5] (vs. Li/Li$^+$), leading to ethylene gas evolution at the graphite electrode surface accompanied by Li$_2$CO$_3$ formation [6]. Evidence of the presence of inorganic products such as Li$_2$CO$_3$, PO$_2^-$ and PO$_3^-$ in the SEI layer has been provided by the observation of a series of small bands within the 1100-1084 cm$^{-1}$ Raman spectra range [7]. In addition to Raman spectroscopy, a variety of other experimental techniques have been used to characterize the SEI layers. These techniques have been summarized in a recent review [8]. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) have indicated the presence of lithium alkyl carbonates (R-O-OCO$_2$Li) and lithium alkoxides (R-OLi) within the SEI [9]. However, these techniques have limitations as the highly energetic beam spot in XPS could lead to the degradation of the SEI components, altering their chemical composition while the FTIR only detects the infrared active components. The use of TOF-SIMS [10] has suggested that the composition of SEI might incorporate Li, F, O, C and H with micro-phase sizes of less than 1 μm. AFM (in situ) measurements [6], used to study SEI formation on highly oriented pyrolytic graphite (HOPG) electrodes, have revealed the formation of an SEI with a thickness of about 20 nm that uniformly covered the graphite surface.

In addition to affecting electron transport and Li$^+$ diffusion kinetics, the formation of SEI influences the fracture and delamination (or exfoliation) type damage of the underlying graphite electrode. Using SEM observations, it has been reported that the graphite exfoliation would lead to an enlargement of the electrode surface area in contact with the electrolyte [11]. The enhanced contact between the electrode and the electrolyte was suggested to cause an increase in the irreversible charge loss and consequently resulted in electrode failure. Evidence of the fracture of graphite particles and fragmentation during cycling was provided by ex-situ Raman spectroscopy studies [12]. The delamination of
graphite layers occurred preferentially adjacent to SEI/graphite interfaces and attributed to the formation of interlayer cracks [13]. Additionally, Li₂CO₃ and Li₂O were observed on the surfaces of these cracks. SEI formation has also been perceived to reduce the propensity of graphite fracture [14]. A uniform and continuous SEI, formed during low scan rate tests (0.05 mVs⁻¹), was suggested to be necessary to reduce graphite damage [15].

To rationalize the SEI formation mechanism, it is important to consider the role of Li⁺ diffusion at the electrode/electrolyte interface. The Li⁺ diffusion rate could play a critical role in determining the composition and morphology of the SEI during its formation. The diffusion coefficient of Li⁺ ($D_{Li^+}$) can be determined using cyclic voltammetry (CV) and analyzing the data by the Randles-Ševčík method [16]. The values of $D_{Li^+}$ were measured by means of other electrochemical techniques including potential intermittent titration, current pulse relaxation (CPR), potential step chronoamperometry (PSCA) and electrochemical impedance spectroscopy (EIS). The measured values varied over a broad range between $10^{-6}$ and $10^{-10}$ cm²s⁻¹ within the various carbonaceous materials used in these tests [17-19]. For example, using EIS a $D_{Li^+}$ value of $10^{-6.4}$ cm²s⁻¹ was measured for carbon fibers [17] that was several magnitudes higher than those obtained by CPR and PSCA ($D_{Li^+} = 10^{-12}$ cm²s⁻¹ [18]). CV test results correlated with numerical models [19] determined a $D_{Li^+}$ of $10^{-10}$ cm²s⁻¹ for carbon fiber electrodes. Dissimilarities in electrode thickness, porosity and particle shape are among the factors that can account for the large variation in the reported $D_{Li^+}$ values. It was predicted that the surface structure of the electrode could influence the activation energy for Li⁺ transfer at the electrode/electrolyte interface [20].

The objectives of this work are twofold. First, in light of the experimental studies reviewed above, certain aspects of SEI composition and microstructure have been
understood; yet there remains a need for direct observation of the microstructure and morphology of the SEI using microscopic methods. This type of information could be best provided by high-resolution transmission electron microscopy (HR-TEM) techniques and through the examinations of cross-sections taken from the SEI/graphite interfaces. For this purpose, a focused ion beam (FIB)-milled, cross-sectional sample preparation methodology has been used in this work to study the subsurface features of electrochemically cycled graphite electrodes. Second, the dependence of SEI formation on the applied voltage and scan rates was investigated by performing voltammetry experiments that helped analyze the Li\(^+\) diffusion kinetics operating at different scan rates. The combined analyses of electrochemical kinetics results and the microstructural observations shed light on the morphology of SEI formed at different voltage scan rates in addition to revealing critical details about the compositions and microstructures of the components present in the SEI layers.

4.2. Experimental

4.2.1. Description of material and electrochemical tests

Linear sweep voltammetry tests were performed using a Potentiostat/Galvanostat system (Solartron Modulab System with a high-speed data acquisition rate of up to 1 MSs\(^{-1}\)) that operated between 3.00 and 0.02 V (vs. Li/Li\(^+\)) using different scan rates between 0.50 and 5.00 mVs\(^{-1}\). The graphite used to fabricate the cylindrical anodes with a diameter of 5 mm was 99.999% pure and contained trace elements of Al, Fe, Mg and Si (~ 10 ppm). Fig.4.1 (a) shows an SEM image of the graphite electrode surface. X-ray diffraction (XRD) spectrum of the graphite is shown in Fig.4.1 (b).
Fig. 4.1. (a) An SEM (FEI Quanta 200 FEG) image of a graphite electrode surface before cycling showing the presence of porosities. (b) An XRD spectrum of the electrode surface obtained using a Bruker-AXS D8 diffractometer set to grazing incidence mode (incident angle, $\omega = 1^\circ$). (c) 3-dimensional optical surface profilometry image of graphite electrode surface obtained using WYKO NT 1100, showing the surface morphology of the graphite.

The polycrystalline nature of graphite was indicated by the sharp intensity of the XRD peaks, namely, the (002) reflection at $2\theta = 26.4^\circ$. Reflections from (100), (101) and (004) sets of planes of graphite were also observed as has been reported previously [21,22]. The graphite crystallite size ($L_{c,002}$), determined using the Scherrer equation ($L_{c,002} = 0.9\lambda/B\cos\theta$; where $\lambda = 1.54$ Å is the wavelength of Cu-K$\alpha$ radiation, and $B$ is the full width
at half the maximum intensity of the (002) in radians), was 40 nm. The grain size was also measured as 25.74±10.9 nm from the cross-sectional TEM (JEOL 2010F STEM) images that exhibited randomly distributed nanometer-sized grains. Thus, the microstructure of the material was consistent with that of bulk, polycrystalline graphite. Using ASTM C373-88 specifications [23], the apparent specific gravity of the graphite electrode was calculated as 2.2, and the bulk density as 2.1 gcc⁻¹. The volume of open pores was 4.1×10⁻³ cc, whereas the apparent porosity was 4.56%. The surface of a pristine graphite electrode observed using optical surface profilometry (WYKO NT1100) is shown in Fig.4.1 (c). The average surface roughness of the graphite electrodes was 135.87±3.7 nm, according to optical profilometer data recorded from an area of 50×50 µm², indicating that the graphite surface was non-faceted and optically flat.

The graphite electrode was cleaned ultrasonically using acetone and placed at the centre of an electrochemical cell. The cell, constructed from polytetrafluoroethylene (PTFE), was assembled and sealed in an Ar-filled MBraun LABstar workstation with H₂O and O₂ levels maintained below 1 ppm. A quartz (optical) glass window was installed at the top of the cell for graphite surface observation by an optical microscope during the test. Details of the experimental setup are given in [13]. A 99.99% pure lithium wire with a resistivity of 9.446 µΩ-cm (at 20°C) was used as the counter electrode. The reference electrode was also made of 99.99% pure lithium wire. The electrolyte solution was formed using 1 M LiClO₄ (99%) in a 1:1 (by vol.) mixture of ethylene carbonate (EC, 99%) and 1,2-dimethoxy ethane (DME, 99+% stabilized with 0.01% butylated hydroxytoluene).
4.2.2. Solid electrolyte interphase characterization techniques

The surface morphologies of the graphite electrodes before and after each electrochemical test were observed using a FEI Quanta 200 FEG Scanning Electron Microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). The cycled electrodes were washed in the electrolytic solution prior to placing them in the SEM. Two-dimensional elemental distribution maps of the graphite surface were obtained at 10 kV using the EDS with a dwell time of 200 µs and a spot size of 3.9.

Cross-sectional samples were excised perpendicular to the SEI/graphite electrode interface using focused ion beam (FIB) milling techniques for both the SEM and TEM examinations. A trench was milled normal to the SEI/graphite interface using Ga⁺ ions sputtered at an accelerating voltage of 30 kV and a beam current of 13.0 nA. The surfaces of the sections were protected from ion-beam damage by depositing a carbon layer prior to milling. The final milling of the cross-sectional sample was conducted using a low ion-beam current of 6.5 nA. A Zeiss NVISION 40 dual beam SEM/FIB was used to investigate the cross-sectional microstructure of the SEI layers at an operating voltage of 5.0 kV.

The cross-sectional samples used in the TEM investigations were milled from both sides to a thickness of 2 µm under a low beam current and removed using the FIB in-situ “lift-out” technique. Details of sample preparation steps are given in [13]. A JEOL 2010F STEM was used to observe the microstructures of cross-sectional samples at an operating voltage of 200 kV. A FEI Titan 80-300 TEM equipped with a hexapole-based aberration corrector for the image-forming lens and a lateral resolution < 1 Å was operated at 300 kV to obtain high-resolution images of the SEI layers.
Raman spectra were collected from selected locations on the surfaces of the cycled electrodes to determine the compositions of inorganic/organic components present in the SEI. A 20 mW He-Ne laser emitted at the 514.5 nm excitation line was employed to excite the sample through the 50× objective lens of a Renishaw inVia Raman microspectrometer. The diameter of the laser spot on the specimen surface was 1 μm (for 50× objective lens) and the effective power of the incident laser was 2.5 mW.

4.3. Results

4.3.1. Linear sweep voltammetry at different scan rates

Linear sweep voltammetry tests were performed starting from a voltage of 3.00 V and continued at a constant scan rate until a low voltage of 0.02 V (vs. Li/Li+) was reached. Several different scan rates ranging between 0.05 and 5.00 mVs⁻¹ were used in the same voltage range, between 3.00 and 0.02 V. The variation of current densities \( i/A \), where \( A = \) electrode surface area) for each test was plotted against the voltage (vs. Li/Li+) as shown in Fig.4.2. The voltammetry curves revealed the formation of scan peaks \( v_p \) at different voltage values with changes in the voltage scan rates. The voltage peaks were observed to appear within the voltage range of \( v_p = 0.43 \) V (at 5.00 mVs⁻¹) to 0.75 V (at 0.05 mVs⁻¹).

In potentiodynamic tests, voltage scan peaks were typically observed to occur during the first cycle within the voltage range of 0.30 and 0.80 V [5] (vs. Li/Li⁺) and their occurrence was attributed to the reduction of EC accompanied by ethylene gas evolution [24]. In this case, the \( v_p = 0.75 \) V value observed at the lowest scan rate of 0.05 mVs⁻¹ was comparable to that reported for EC reduction. The \( v_p \) values, along with their corresponding peak current densities \( i_p/A \), are reported in Table 4.1.
Fig. 4.2. Plots of current density against voltage (vs. Li/Li⁺) obtained from linear sweep voltammetry tests performed on graphite anodes from 3.00 V to 0.02 V at sweep rates from 0.05-5.00 mVs⁻¹. The scan peaks, attributed to solvent reduction during each test, have been indicated by arrow marks. The voltage and current density values corresponding to each peak have been tabulated in Table 4.1.

The value of \( v_p \) decreased with the increase in \( \frac{dV}{dt} \). For example, \( v_p \) was 0.75 V at 0.05 mVs⁻¹, whereas a \( v_p \) of 0.57 V was observed at 0.50 mVs⁻¹. In contrast, the magnitude of \( i_p/A \) was observed to increase with \( \frac{dV}{dt} \). The current density in voltammetric experiments with graphite negative electrodes is controlled by Li⁺ diffusion [25]. In high \( \frac{dV}{dt} \) tests, the high \( i_p/A \) observed can be attributed to faster Li⁺ insertion kinetics [26] during SEI formation. Therefore, a plot of \( i_p/A \) against \( \frac{dV}{dt} \) can be used to determine changes in the
Li$^+$ diffusion coefficient and will be discussed further in Section 4.4.1. The following section describes the changes in the morphological features of SEI layers formed on the graphite surface with variations in the applied $dV/dt$.

Table 4.1 – Peak current density ($i_p/A$) and voltage ($v_p$) values observed during linear sweep voltammetry tests performed from $V = 3.00$ V $\rightarrow$ 0.02 V at $dV/dt = 0.05-5.00$ mVs$^{-1}$.

<table>
<thead>
<tr>
<th>Scan rate ($dV/dt$), mVs$^{-1}$</th>
<th>Peak voltage ($v_p$, V)</th>
<th>Peak current density ($i_p/A$, mAcm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.75</td>
<td>0.97</td>
</tr>
<tr>
<td>0.10</td>
<td>0.68</td>
<td>1.71</td>
</tr>
<tr>
<td>0.50</td>
<td>0.57</td>
<td>4.18</td>
</tr>
<tr>
<td>1.00</td>
<td>0.56</td>
<td>5.89</td>
</tr>
<tr>
<td>2.00</td>
<td>0.47</td>
<td>8.34</td>
</tr>
<tr>
<td>3.00</td>
<td>0.49</td>
<td>9.74</td>
</tr>
<tr>
<td>4.00</td>
<td>0.46</td>
<td>15.31</td>
</tr>
<tr>
<td>5.00</td>
<td>0.43</td>
<td>16.88</td>
</tr>
</tbody>
</table>

4.3.2. Description of solid electrolyte interphase formed on graphite surface at different scan rates

The changes induced on the surfaces of graphite electrodes cycled at 0.05 mVs$^{-1}$ are shown as a back-scattered (BS)-SEM image in Fig.4.3 (a) along with its corresponding EDS map in Fig.4.3 (b) showing the distribution of the elements of interest: carbon, oxygen and chlorine. The EDS map confirmed that the deposits were rich in oxygen and chlorine. These deposits were identified as SEI since oxygen is a component of LiClO$_4$ (electrolyte salt), Li$_2$CO$_3$ and Li$_2$O$_2$ (formed during electrochemical reduction as reported in Section 4.3.3) and chlorine is a component of LiClO$_4$. For the test performed at 0.10 mVs$^{-1}$, the surface changes are shown as a BS-SEM image in Fig.4.3 (c) and an EDS map in Fig.4.3 (d). After scanning at 5.00 mVs$^{-1}$, the resulting BS-SEM image of the cycled graphite surface is shown.
Fig. 4.3. Back-scattered (BS)-SEM images with corresponding EDS elemental maps (with red indicating graphite, oxygen represented by yellow and chlorine by blue; color available in online version) depicting changes in graphite electrode surfaces cycled from 3.00 to 0.02 V at scan rates of ((a) and (b)) 0.05 mVs\(^{-1}\), ((c) and (d)) 0.10 mVs\(^{-1}\), and ((e) and (f)) 5.00 mVs\(^{-1}\). Oxygen is a component of LiClO\(_4\) (electrolyte salt), Li\(_2\)CO\(_3\) and Li\(_2\)O\(_2\) (formed during electrochemical reduction as reported in Section 4.3.3) and chlorine is a component of LiClO\(_4\).
in Fig.4.3 (e) with its EDS map shown in Fig.4.3 (f). Exposed graphite was depicted by portions of dark contrast in the BS-SEM image, whereas regions of slightly lighter contrast indicated the existence of deposits on top of the graphite. The area fraction of SEI covering the graphite surfaces was determined by an image processing and analysis program (ImageJ, Version 1.45s, developed at the National Institutes of Health, USA). The BS-SEM images were first converted to 8-bit grayscale images. The image conversion was followed by thresholding, performed in the black-and-white channel, which enabled outlining of the SEI. Lastly, the area fraction of SEI was determined using the measuring function of the ImageJ toolkit. An examination of the graphite electrode cycled at a low scan rate of 0.05 mV s\(^{-1}\) is shown in Fig.4.3 (b). Other images taken from the same electrode depicted that a large portion of the graphite surface was covered by SEI deposits. Specifically, the SEI covered as much as 75\% of the exposed graphite. At a slightly higher scan rate of \(\frac{dV}{dt} = 0.10\) mV s\(^{-1}\), the area percentage of SEI on the graphite surface decreased to 65\% [Fig.4.3 (d)]. With a further increase of \(\frac{dV}{dt}\) to 5.00 mV s\(^{-1}\), the SEI deposits covered only 35\% of the graphite surface, with large regions of exposed graphite surface easily observed in Fig.4.3 (f). Further evidence of the dependence of thickness and uniformity of the SEI deposits on was provided by the cross-sectional microstructures of cycled graphite electrodes, and will be described in detail in Section 4.3.3.

### 4.3.3. Morphology and microstructure of solid electrolyte interphase

The cross-sectional microstructures of electrodes demonstrated the differences in SEI morphologies as formed at high and low voltage scan rates. The SEI that was formed at a low scan rate of 0.05 mV s\(^{-1}\) consisted of deposits that covered the graphite surface more uniformly than those formed at higher scan rates. As seen in Fig.4.4 (a), the graphite subsurface consisted of a few pre-existing porosities and was unaffected by cycling due to
the formation of the SEI deposits. The SEI deposits were well-adhered to the graphite surface in the form of a continuous layer. No defects or cracks were observed at the interface between this layer and the graphite. The average thickness of the layer was quite uniform in the range of $1.02\pm0.15\ \mu m$. At high magnification, the SEI layer displayed a uniform distribution of tubular structures that were either standing alone or connected to each other, as seen in Fig. 4.4 (b). These structures were usually intertwined, and the presence of occasional spherical particles was also noted.

Fig. 4.4. (a) FIB-milled, cross-sectional microstructure of a graphite electrode cycled from $V = 3.00 \rightarrow 0.02 \ \text{V at } 0.05 \ \text{mVs}^{-1}$; (b) SEI deposits formed on the graphite surface at $0.05 \ \text{mVs}^{-1}$; (c) FIB-milled, cross-sectional microstructure of a graphite electrode cycled at $5.00 \ \text{mVs}^{-1}$ in the same range as (a), and (d) SEI deposits formed on graphite surface at $5.00 \ \text{mVs}^{-1}$.

The SEI deposits that were formed on a graphite surface at a high scan rate of $5.00 \ \text{mVs}^{-1}$ [Fig. 4.4 (c)] were much less uniform in thickness and featured large regions of
exposed graphite surface. A high magnification SEM image of the deposits, seen on the graphite surface in Fig.4.4 (c), is presented in Fig.4.4 (d). In this case, the SEI deposits formed a unidirectional columnar structures; the growth direction of the columns being perpendicular to the graphite surface. In certain locations, the column height reached 2.90 μm (indicated as A in Fig.4.4 (d)), whereas in other locations their heights were limited to 0.49 μm (indicated as B in Fig.4.4 (d)). Regions of exposed graphite were located between the columnar deposits.

Compositional analyses of the SEI deposits on these electrode surfaces were provided using micro-Raman spectroscopy. Fig.4.5 (a) is a Raman spectrum obtained from a pristine graphite surface and the spectrum in Fig.4.5 (b) was obtained from a graphite electrode cycled between 3.00 and 0.02 V at a linear scan rate of 5.00 mVs⁻¹ for 50 cycles. In the Raman spectra of carbon and its allotropes, the G-band appearing at 1580 cm⁻¹ [Figs.4.5 (a) and (b)] is attributed to the \( \text{sp}^2 \)-type binding of carbon atoms, whereas the D-band observed at 1350 cm⁻¹ is associated with the structural characteristics of the graphite surface [27]. The Raman spectra also detected the presence of organic/inorganic components deposited on the graphite surface as a result of lithium-ion cell cycling. No evidence of chemical compounds was found within the graphite surface before electrochemical cycling [Fig.4.5 (a)]. However, a couple of low intensity peaks near 950 and 1085 cm⁻¹ were observed in the Raman spectrum obtained from the cycled graphite surface [Fig.4.5 (b)] due to the symmetric stretching vibrations [7] of Li₂CO₃. The presence of Li₂CO₃ indicated the occurrence of EC reduction on the graphite surface (Section 4.3.1). Further crystallographic information on Li₂CO₃ was obtained by performing high resolution (HR)-TEM that also identified other lithium compounds.
Fig. 4.5. Raman spectra obtained from (a) pristine graphite and (b) the graphite electrode cycled between 3.00 and 0.02 V at a linear scan rate of 5.00 mVs⁻¹ for 50 cycles. Multiple low intensity peaks close to 950-1085 cm⁻¹ indicate the presence of Li₂CO₃ on the graphite surface.

The cross-sectional microstructure of the graphite electrodes adjacent to the interface with the SEI was subjected to TEM observations in order to study the changes that occurred in the crystalline structure of the graphite. The TEM observations were carried out using cross-sectional samples prepared by means of the FIB in situ “lift-out” technique as described in Section 4.2.2. The dark-field TEM image in Fig.4.6 (a) shows that the microstructure of the graphite, near the SEI/graphite interface consisted of equiaxed nanometer-sized grains (grain size= 25.74±10.9 nm) that were randomly oriented. The average grain size was similar to the ones observed in pristine graphite electrodes (Section 4.2.1). These grains were observed to have a particular crystallographic orientation, namely {100}, as indicated in the selected area diffraction pattern (SADP) provided in Fig.4.6 (b). For calculating the d-spacings corresponding to each diffraction spot in Fig.4.6 (b), an image processing and analysis program, UTHSCSA ImageTool (IT) equipped with median filtering.
and spatial convolutions with user-defined convolution masks, was used. Using this program, the measurement of the interplanar distances was repeated at least five times and each time determined to an accuracy of two decimal places. The mean value of the five readings was reported for each diffraction spot. Diffraction spots in the SADP obtained from the \{002\} family of graphite planes indicated a \(d\)-spacing of 0.349±0.003 nm. The \(d\)-spacing for the \{002\} planes in the same graphite electrode was measured as 0.34 nm [28] in the pristine condition. The increase in \(d\)-spacing of graphite electrode's crystal planes after the electrochemical cycling process could possibly be attributed to the lithiation of graphite [29]. In addition, analyses of the other diffraction spots observed in the SADP, revealed

\textbf{Fig.4.6.} (a) Dark-field TEM image acquired using \{100\} diffraction beam of the (b) selected area diffraction pattern showing randomly oriented nanometer-sized graphite grains near the SEI/graphite interface. Diffraction spots corresponding to the \{002\} planes of graphite, \{110\} planes of Li\(_2\)CO\(_3\) and \{101\} planes of Li\(_2\)O\(_2\) were also observed. (Carbon was deposited during the TEM sample preparation prior to FIB-milling.)
presence of crystallographic planes with \(d\)-spacings of 0.42 nm which corresponded to the \{110\} planes of Li\(_2\)CO\(_3\) [30]. Diffraction spots corresponding to a \(d\)-spacing of 0.25 nm were also observed which were identified as the \{101\} planes of Li\(_2\)O\(_2\) [31].

Detailed microstructural characterization of the SEI layers was carried out by conducting high magnification TEM observations of the SEI at locations near the SEI/graphite interface. A bright-field TEM image of the interface between the SEI layer and graphite planes is shown in Fig.4.7 (a). The morphology of the SEI observed at this magnification appeared to consist of submicroscopic SEI-forming particulates and granules that were well adhered to the graphite surface. Fig.4.7 (b) is a high resolution (HR)-TEM image obtained from the interference pattern of the electron beams that are transmitted and diffracted [32,33] through the area marked as (b) in Fig.4.7 (a), adjacent to the interface. The image provides evidence for crystalline domains within an amorphous matrix. Specifically, crystalline domains of \(\sim 5-20\) nm in size are shown in Fig.4.7 (b) where the presence of distinct lattice planes (in regions (c) and (d)) reveal regular interplanar spacings. The lattice planes of these crystalline domains were further analyzed by means of reduced fast Fourier transform (FFT)-derived diffraction patterns in Figs.4.7 (c)-(e). The FFT-derived diffraction pattern in Fig.4.7 (c) identified the presence of lithium compounds in a typical crystalline region marked as (c) in Fig.4.7 (b). An analysis of Fig.4.7 (c) indicates that the diffraction spots could be identified as Li\(_2\)CO\(_3\) based on the reflections from the \\{31 \(\bar{T}\)\} planes with a \(d\)-spacing of 0.24 nm. Thus, this analysis provided complementary evidence for the presence of Li\(_2\)CO\(_3\) on the graphite surface (and within the graphite layers underneath the interface as in Fig.4.6) that micro-Raman spectroscopy detected earlier. Similarly, Li\(_2\)O\(_2\) was also be identified based on the reflections of the \{201\} or \{105\} planes with a \(d\)-spacing of 0.13 nm.
These were accompanied by the reflections from \{100\} \(d_{100} = 0.21\) nm and \{102\} \(d_{102} = 0.17\) nm family of graphite planes.

An interesting observation pertaining to graphite was found in the FFT-pattern obtained from the area marked as (d) in Fig. 4.7 (b) and shown in Fig. 4.7 (d). Diffraction spots corresponding to the same \{100\} crystallographic planes of graphite were detected, but these planes had different orientations. This observation can be attributed to graphite nano-crystals that were present in the SEI layers. Accordingly, this suggests that the graphite particles were removed from the electrode and mixed with the lithium compounds in the

![Fig.4.7.](image)

Fig.4.7. (a) A high magnification cross-sectional bright-field TEM image of a graphite electrode cycled between 3.00 V and 0.02 V at a scan rate of 0.05 mV s\(^{-1}\) showing \{002\} graphite layers running parallel to each other and merging with the electrode/electrolyte interface. The SEI at the interface displayed a granular appearance. The \{002\} direction was determined by the orientation of the \(g_{002}\) vector.
Fig. 4.7. (b) HR-TEM image obtained from the interference pattern of the electron beams that are transmitted and diffracted through a region at the interface, indicated as region (b) in plate (a), revealing the crystalline and amorphous regions of the solid electrolyte layer. Reduced FFT-derived diffraction patterns showing (c) the presence of lithium compounds, Li$_2$CO$_3$ and Li$_2$O$_2$, in a typical crystalline region marked as (c) in plate (b); (d) reflections from nano-fragments of graphite from a region marked as (d) in (b), and (e) a diffused halo corresponding to an amorphous region marked as (e) in plate (b).
SEI. The FFT-derived diffraction pattern obtained from a third region of interest in Fig.4.7(b) (marked as (e)) and shown in Fig.4.7 (e) revealed the presence of a diffuse diffraction halo, indicating that an amorphous structure surrounded the crystalline domains.

4.4. Discussion

Section 4.3 depicted that the morphology, thickness and uniformity of the SEI deposits depended on the applied voltage scan rates. The SEI was found to consist of lithium based compounds and graphite nano-crystals within crystalline domains surrounded by an amorphous regime. This section discusses the possible cause of variations in the SEI morphology due to changes in scan rate. The SEI formation mechanism has been subsequently analyzed.

4.4.1. Effect of Li⁺ diffusion kinetics on solid electrolyte interphase formation

According to the results presented in Section 4.3.2 when the voltammetry tests were carried out at low scan rates, a larger fraction of the graphite surface area was covered by SEI deposits compared to those tested at higher scan rates. This variation in SEI distribution on the graphite surface can be discussed in terms of the differences in the Li⁺ diffusion kinetics which, in turn, depends on the scan rate, \( \frac{dV}{dt} \). Voltammetry experiments conducted at different scan rates suggested that the Li⁺ diffusion kinetics could be analyzed in the formalism of the Randles-Ševčík method [25,34]. As described in Section 4.3.1, considering that the peak current density \( i_p \) varies with the \( \frac{dV}{dt} \), the following relationship could be established:

\[
\frac{i_p}{A} = 2.69 \times 10^5 n^2 C_{Li}^{\frac{3}{2}} D_{Li} \left( \frac{dV}{dt} \right)
\]  

(4.1)

where, \( A (= 19.625 \text{ cm}^2) \) is the electrode area, \( n (= 2 [6,35]) \) is the number of electrons
transferred in the electrode reaction, and \( C_{Li} (= 106.4 \times 10^{-3} \text{ mol cm}^{-3}) \) is the concentration of the electro-active species (LiClO\(_4\)) in the electrolyte. Accordingly, the diffusion coefficient of Li\(^+\) (\( D_{Li}^{+}, \text{cm}^2\text{s}^{-1} \)) can be calculated from the slope of the linear relationship obtained when \( i_p \) is plotted against \((dV/\text{dt})^{0.5}\) using the experimentally determined values listed in Table 4.1. Two diffusion regimes become evident that are distinguished by different slopes as shown in Fig.4.8; at high \( dV/\text{dt} \), the rate of Li\(^+\) diffusion was high with a \( D_{Li}^{+} = 3.13 \times 10^{-8} \text{ cm}^2\text{s}^{-1} \). For low scan rates, Fig.4.8 indicates that \( D_{Li}^{+} \) was \( 0.57 \times 10^{-8} \text{ cm}^2\text{s}^{-1} \) which was comparable to diffusion coefficient values reported previously [36-39]. The transition between the two \( D_{Li}^{+} \) regimes occurs at \( dV/\text{dt} = 3.00 \text{ mVs}^{-1} \).

---

**Fig.4.8.** Plot showing changes in the Li\(^+\) diffusion coefficient (\( D_{Li}^{+} \)), calculated based on the Randles-Ševčik relationship between peak currents (\( i_p \)) and the square root of potential scanning rates (\( dV/\text{dt} \)).
The dissimilarities in the SEI morphologies at different scan rates, prompting two different Li\(^+\) diffusion regimes, could be attributed to different atomic mechanisms by which the electrolyte molecules attached themselves to the interface with graphite electrode. At the SEI forming potential, the diffusion of electrolyte molecules occurred by their advancement towards the electrode surface. At \(dV/dt = 5.00 \text{ mVs}^{-1}\), the graphite surface was subjected to the electrochemical reduction process for only a very short time of \(0.06 \times 10^4 \text{ s}\). In this case, the SEI layer formation was incomplete and the graphite surface exhibited large regions devoid of SEI. Only 35% of the graphite surface was covered by SEI [Fig.4.3 (f)]. Thus, high Li\(^+\) diffusion rates led to the formation of a non-uniform SEI layer, with unidirectional columnar structures [Fig.4.4 (d)], on the initially non-faceted electrode surface. Therefore, the graphite electrode surface was exposed to further cycling-induced damage. A typical example of damaged graphite after voltammetry tests is shown in Fig.4.9. The cross-sectional SEM image shows parallel-running graphite cracks that propagated obliquely to the SEI/graphite interface for 0.5-2.0 \(\mu\text{m}\). The non-uniform morphology of the SEI formed at the interface can also be seen.

![Cross-sectional SEM image](image)

**Fig.4.9.** Cross-sectional SEM image of the subsurface region of a graphite electrode showing the presence of cracks at the SEI/graphite interface.
On the other hand, when a low $dV/dt$ of 0.05 mVs$^{-1}$ was applied, a uniform SEI layer was formed [40] as sufficient time (5.96×10$^4$ s) was available for the reduction reactions to occur. In this case, the area percent of SEI covering the graphite surface was as large as 75% [Fig.4.3 (b)]. The SEI layer, with a uniform distribution of tubular structures [Fig.4.4 (b)], was capable of protecting the graphite surface effectively [15] and prevented delamination or exfoliation [11,41]. It could be suggested that a low $dV/dt$ was conducive to establishing conditions that were favorable for steady Li$^+$ diffusion at the electrode/electrolyte interface.

In summary, the diffusion of Li$^+$ at the SEI/graphite interface during SEI formation, controlled by the applied $dV/dt$, dictated the morphology and thickness of the SEI. In these experiments the initial graphite structure [Fig.4.1 (c)] had a non-faceted surface morphology and was optically flat. In commercial lithium-ion batteries, flaky or spherical graphite particles, used as anodes, possess faceted surfaces [42,43] that would promote the formation of a non-uniform SEI with columnar structures even under conditions of slower Li$^+$ diffusion kinetics. The graphite particles or flakes are, therefore, susceptible to degradation as a non-uniform, columnar SEI is not effective for protecting the graphite particles. Further details of the constituents of a stable SEI have been discussed in Section 4.4.2.

4.4.2. Micromechanisms of solid electrolyte interphase formation

The mechanisms of SEI formation on graphite electrodes that emerged from this study are shown schematically in Fig.4.10; SEI coverage of the graphite surface depended on the diffusion of Li$^+$ (reflected by the $D_{Li^+}$ value) operating at the electrode/electrolyte interface during the electrochemical reduction of ethylene carbonate. A low rate of Li$^+$
diffusion accompanied by solvent co-intercalation during the reduction process enabled the formation of a stable SEI.

According to the analyses of the high resolution cross-sectional TEM images (Section 4.3.3) SEI consisted of nanocrystalline structural domains distributed in an amorphous matrix. These crystalline domains had interplanar spacings corresponding to lithium based compounds of Li₂CO₃ and Li₂O₂. Additionally, nanoparticles of graphite were detected (Figs.4.7 (c) and (d)) that could have formed as a result of delamination or fragmentation of graphite electrodes. The cracks that are responsible for the delamination of graphite layers at the SEI/graphite interface are shown in Fig.4.9. In addition, formation of
surface and near surface cavities within graphite electrodes were reported previously [14,44].

One possible consequence of cycling-induced graphite particle fragmentation would be enhancement of phonon scattering at the SEI/graphite interface. This, in turn, would manifest itself by the intensification of D-band peak in Raman spectra of exposed graphite. In fact, the Raman spectrum obtained from a graphite electrode after scanning at a high rate of 5.00 mVs⁻¹ for 50 cycles [Fig.4.5 (b)] depicted a higher relative intensity for the D-band than for the G-band (1580 cm⁻¹), indicating an increase in the degree of disorder (= I_D/I_G) from 0.53±0.05 (pristine) to 1.015±0.13 (cycled) during electrochemical cycling.

4.5. Conclusions

This study explored the formation of solid electrolyte (SEI) layers on graphite electrodes cycled in lithium-ion cells as a function of the applied voltage scan rates, and their morphologies, microstructures and compositions were determined. The main conclusions can be summarized as follows:

1. Application of low voltage scan rates caused the formation of a uniform and dense SEI layer that covered most of the graphite electrode surface. However, with an increase in the applied scan rates, the SEI layer became less uniform in thickness and distribution leaving large regions of graphite electrode surface exposed.

2. The microstructure of the SEI consisted of nano-crystalline domains of ~ 5-20 nm in size dispersed within an amorphous structure. Within these crystalline domains, nano-sized graphite fragments were mixed with the decomposition products of the SEI layers, namely, Li₂CO₃ and Li₂O₂.

3. The applied voltage scan rate controlled the Li⁺ diffusion kinetics at the electrode/electrolyte interface which, in turn, induced variation in SEI distribution on
the graphite surface. At higher scan rates ($\geq 3.00 \text{ mVs}^{-1}$), the coefficient of Li$^+$ diffusion ($D_{\text{Li}}$) was $3.13\times10^{-8} \text{ cm}^2\text{s}^{-1}$ that resulted in an incomplete SEI layer formation and the graphite surface exhibited large regions devoid of SEI prone to further electrochemical reduction. In contrast, a low $D_{\text{Li}}$ of $0.57\times10^{-8} \text{ cm}^2\text{s}^{-1}$ prompted conditions that were favorable for producing a stable SEI beneficial for improved cyclic performance of graphite electrodes.

**Bibliography**


CHAPTER 5: Thermal Cycling Induced Capacity Enhancement of Graphite Anodes in Lithium-ion Cells

5.1. Introduction

The performance of Li-ion cells, such as their charge/discharge capacity and cyclability are strongly affected by the degradation of the electrode materials [1-4], and the nature (i.e. composition, morphology and stability) of the solid electrolyte interphase (SEI) layer [5] that forms on their surfaces. In fact, SEI often plays a positive role and may reduce exfoliation or delamination-type damage of the underlying graphite electrode [6,7]. The effectiveness of the SEI in reducing graphite damage depends on the morphology and composition of this layer. It was observed that during low scan rate tests (0.05 mVs⁻¹), a uniform and continuous SEI that was formed with a tubular morphology [6] was effective in lessening graphite damage [8]. Graphite surface damage by cavitation—due to removal of the surface graphite fragments of 5-10 μm size—is the most intense during the first cycle. Cavities were observed as dark spots under the optical microscope and subsequently their morphologies were confirmed by SEM [7]. Once the SEI layer forms, the intensity of cavitation-induced graphite degradation decreases [9,10]. But still delamination of graphite layers could proceed by the formation of interlayer cracks adjacent to SEI/graphite interfaces [7]. Co-intercalation products like Li₂CO₃ and Li₂O were observed on the crack surfaces. Evidence of graphite damage by fragmentation was provided by Raman spectroscopy and atomic force microscopy (AFM) studies [11-13] as well as by high-resolution optical microscopy [9] conducted during cycling.

There is scattered evidence about the role of SEI on electrode damage at elevated temperatures. The metastable components of SEI like lithium alkoxides (R-OLi) and lithium
alkyl carbonates (R-OCO₂Li) are believed to become unstable at temperatures typically exceeding 60°C—for LiBF₄ containing electrolytes [14], 105°C—for LiPF₆ containing electrolytes [15], and may convert to a stable compound, Li₂CO₃ [16]. It has been stated that the SEI growth is significant at temperatures between 60-130°C [17-19]. For example, the thickness of the SEI layer on the surfaces of highly oriented pyrolytic graphite (HOPG) electrodes increased with the temperature, from 16 nm at 30°C to 150 nm at 80°C, in an ethylene carbonate solution [20]. At 80°C, enhanced solvent decomposition and subsequent accumulation of the inorganic products on graphite particles were cited as a possible reason for the increase in irreversible charge loss [20]. This accelerated the capacity fade and caused exothermic reactions that eventually lead to thermal runaway [21,22]. At temperatures close to 200°C, direct interaction between the graphite and the electrolyte could occur [14,18,23] due to decomposition of the SEI [18,23] and degradation of the electrolyte [15,18]. It has been suggested [24] that electrolyte degradation depends on the magnitude of the energy stored within the cell, the cell temperature and the time duration of exposure to elevated temperatures. Li-ion cells exposed to a temperature of 55°C for a short-term were shown to reduce the amount of stored electrochemical energy and improved the capability of capacity retention [24]. On the other hand, when Li-ion cells were cycled initially at room temperature and then stored at temperatures near 80°C, their capacity declined rapidly, which was attributed to the repeated growth and dissolution of the SEI layer that provided resistance to Li-ion insertion [17,19]. However, the suggested SEI degradation mechanism has yet to be proven. From technological point of view, investigation of high temperature cyclic performance of electrodes in Li-ion batteries is important for two reasons; one is because these batteries are being actively developed for pure and hybrid electric vehicles, as well as for aerospace applications that are required to operate within a broad temperature
range [25-28]. Secondly, understanding of SEI properties and how they influence electrode damage may provide an opportunity to increase battery capacity by means of an electrochemical treatment of the electrodes at elevated temperatures.

Accordingly this work investigates the role of the composition, microstructure and morphology of the SEI that forms on graphite electrodes at elevated temperatures especially between 50 and 60°C and examines the high temperature electrode damage mechanisms. According to previous high-resolution (HR)-TEM studies, the SEI formed on graphite electrodes at 25°C was characterized by crystalline domains, consisting of nano-sized graphite fragments mixed with Li₂CO₃ and Li₂O₂, dispersed within an amorphous structure [6]. Here, the microstructural changes that occurred on the electrode surfaces at 60°C were observed in-situ during voltammetry experiments (vs. Li/Li⁺). The SEI morphology and microstructure adjacent to the SEI/graphite interface were studied using TEM, the chemical compositions of the electrolyte decomposition products were determined using energy-dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). In addition, the rate of Li-ion diffusion during SEI formation was analyzed at different temperatures and its influence on SEI composition was discussed. Once the electrochemical mechanisms that control the SEI structure and morphology and their roles on graphite electrode degradation mechanisms were identified, the results allowed to develop an electrochemical pre-treatment process at 60°C that increased cyclic capacity at 25°C. The micromechanisms responsible for the cyclic capacity enhancement as a result of the thermal pre-treatment were rationalized based on microscopic and spectroscopic investigations.
5.2. Experimental

5.2.1. Description of Materials and Voltammetry Tests

Linear sweep and cyclic voltammetry tests were performed using a Potentiostat/Galvanostat system (Solartron Modulab System with a data acquisition rate of up to 1 MSs⁻¹) that operated between 3.00 and 0.02 V (vs. Li/Li⁺) using scan rates of 0.50, 2.00 and 5.00 mVs⁻¹. The graphite used to prepare electrodes was 99.999% pure and purchased from Kurt J. Lesker, Canada. Using ASTM C373-88 specifications [29], the apparent specific gravity of the graphite was calculated as 2.2, and the bulk density as 2.1×10³ Kg m⁻³. The volume of open pores on the surface was 4.1×10⁻⁹ m³, whereas the apparent porosity of the material was 4.56%. The graphite microstructure revealed the existence of pores and voids that are typically found in turbostratic graphite. Cylindrical electrodes with diameter of 5 mm were prepared from the graphite by micro-wire EDM machining. XRD analyses reported in [6] showed that the graphite had a polycrystalline structure with reflections obtained from (002), (100), (101) and (004) sets of carbon planes. The crystallite size \(L_{c,002}\) was determined as 40 nm from the Scherrer equation \(L_{c,002} = \frac{0.9\lambda}{B\cos\theta}\); where \(\lambda = 1.54\ \text{Å}\) is the wavelength of Cu-K\(\alpha\) radiation, and \(B\) is the full width at half the maximum intensity of the (002) in radians. This was consistent with the TEM (JEOL 2010F STEM) measurement of grain size that was determined as 25.7 ± 10.9 nm [6]. The grains on cross-sectional TEM images were randomly distributed which is a characteristic feature of turbostratic graphite.

A 99.99% pure lithium wire with a resistivity of 9.446 \(\mu\Omega\cdot\text{cm}\) (at 20°C) was used as the counter electrode. The reference electrode was also made of 99.99% pure lithium wire. The electrolyte solution was prepared using 1 M LiClO₄ (99%) in a 1:1 (by vol.) mixture of ethylene carbonate (EC, 99%) and 1,2-dimethoxy ethane (DME, 99+%) stabilized with
0.01% butylated hydroxytoluene). The graphite electrode was cleaned ultrasonically using acetone and placed at the centre of an electrochemical cell with an observation window. The cell, constructed from polytetrafluoroethylene (PTFE), was assembled and sealed in an Ar-filled MBraun LABstar workstation where H₂O and O₂ levels maintained below 1 ppm. An optical in-situ system consisting of a digital microscope with large depth of focus was employed for observation of the progression of graphite surface changes at a magnification as high as 1000× as a function of time and voltage. A schematic representation of the experimental setup is shown in Fig.5.1. The temperature of the cell was controlled using a heater located at the base of the cell and the temperature was maintained within ±1°C of the test temperature.

Fig.5.1. Schematic representation of the experimental setup used for in-situ observation of graphite electrode surface in a Li-ion cell at elevated temperatures using an optical microscope.

5.2.2. Microscopic and Spectroscopic Techniques

The surface morphologies of the graphite electrodes after each electrochemical test were observed using a FEI Quanta 200 FEG Scanning Electron Microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). The cycled electrodes were
washed in the electrolytic solution prior to placing them in the SEM. Two-dimensional EDS maps showing the distribution of the elements on the graphite surface were obtained at 10 kV using a dwell time of 200 μs and a spot size of approximately 3.4 nm.

Cross-sectional samples were prepared by ion-milling of electrodes perpendicular to the electrode surface. Before the ion-milling process the sample surface was sputter coated with an 80-100 nm thick gold protective film using a 10 mA plasma current for 30 s in a compressed argon gas atmosphere with the chamber pressure maintained at 2 mbar. A 1 μm thick tungsten or carbon layer was also deposited (on top of the gold layer) across selected areas where the cross-sectional cuts were made. Cross-sectional samples for both SEM and TEM examinations were excised perpendicular to the SEI/graphite electrode interface using focused ion beam (FIB) milling inside a Zeiss NVISION 40 dual beam SEM/FIB. A trench was milled normal to the SEI/graphite interface using Ga-ions sputtered at an accelerating voltage of 30 kV and a beam current of 13.0 nA. The final milling of the cross-sectional sample was conducted using a low ion-beam current of 6.5 nA and a low voltage of 10 kV. A Zeiss NVISION 40 dual beam SEM/FIB was used to investigate the morphology of the SEI layers and underlying graphite cross-sections.

The cross-sectional samples prepared for the TEM investigations were milled from both sides to a thickness of 100 nm under a low beam current and removed using the FIB in-situ “lift-out” technique. A FEI Titan 80-300 HR-TEM equipped with a Gatan 865 energy filter for EELS was operated at 80 kV to obtain high-resolution imaging of the SEI layers.

Kratos AXIS Ultra X-ray Photoelectron Spectrometer (XPS), equipped with a Magnetic Immersion Lens and Charge Neutralization System with a Spherical Mirror Analyzer, was used to analyze the composition of graphite electrode surfaces. XPS could
probe the electrode surfaces up to a depth of 7-10 nm. Survey scans were carried out with an analysis area of 300×700 μm² using a pass energy of 160 eV, and high resolution analyses were performed on the same area with a pass energy of 20 eV.

Fourier Transform Infrared Spectroscopy (FTIR) was performed using the attenuated total reflection objective on the IRScope II attached to a Bruker IFS-55. On the electrode surfaces, areas with 80-100 μm in diameter and a depth of ~ 2 μm were analyzed. The spectral resolution was 4 cm⁻¹.

5.3. Results

5.3.1. Planar Capacity at Different Temperatures

Planar capacity was calculated for graphite electrodes cycled at 25, 50 and 60°C between 3.00 and 0.02 V using a scan rate of 2.00 mVs⁻¹ by considering the area under the current density (mAcm⁻²) and time (hours) plot for each cycle. At 25°C the capacity dropped from 0.81 mAh cm⁻² in the first cycle to 0.48 mAh cm⁻² in the second cycle, i.e., a decrease of 40% as can be seen in Fig.5.2.

Further cycling did not induce more decrease and the capacity remained fairly constant in the range of 0.53±0.03 mAhcm⁻² for the remainder of ten test cycles. When cycled at 50°C, the capacity drop between the first (3.15 mAh cm⁻²) and second (2.31 mAh cm⁻²) cycles was 27%. Following this initial drop the capacity once again remained constant for the remainder of the test, but at a higher value of 2.26±0.08mAh cm⁻². For the test performed at 60°C, the first cycle capacity was 3.84 mAh cm⁻² and the capacity dropped to 3.18 mAh cm⁻² in the second cycle resulting in a 17% drop that was considerably lower compared to the drop observed at 25°C. During prolonged cycling at 60°C, the planar capacity remained at 3.11±0.12 mAh cm⁻² that was 5.8 times higher than that observed at
25°C (0.53±0.03 mAh cm⁻²). In summary, Fig.5.2 indicates that the capacity loss during initial cycling as well as long-term cyclic capacity improved at 50-60°C. The changes that occurred on the surfaces of the graphite electrode were recorded during cyclic voltammetry tests as described in Section 5.3.2.

**Fig.5.2.** Plot showing the variation of planar capacity with the cycle number during tests conducted at 25, 50 and 60°C.

### 5.3.2. Description of Graphite Electrode Surface Damage and SEI Formation

The surfaces of graphite electrodes were observed in-situ at 1000× magnification using a digital microscope; the surface damage events that occurred during the first cycle of linear sweep voltammetry tests were particularly revealing. Prior to the application of voltage, the pores appear as the darker speckles on the graphite electrode surface in Fig.5.3 (a) before being tested at 25°C. Initially a high voltage of 3.00 V was applied and the voltage was
Fig. 5.3. Optical microstructures (at 1000×) of graphite electrodes obtained in-situ during the first cycle scan from 3.00 V to 0.02 V at 25°C (a) at the beginning of the test (3.00 V) and after reaching (b) 1.00 V, (c) 0.50 V, (d) 0.02 V. Microstructures obtained during tests performed at 60°C for voltages at (e) 3.00 V (f) 1.00 V, (g) 0.50 V and (h) 0.02 V. The scan rate used during the linear sweep tests was 2.00 mVs\(^{-1}\). Comparison of areas marked in the microstructures show enlargement of pre-existing pores and formation of cavities by removal of graphite particles.
decreased at a constant scan rate to 0.02 V (vs. Li/Li⁺). During this process cavities were formed on the electrode surface as a result of the removal of graphite particles from the surface. The number and size of the cavities demarcated by the dark spots increased with the decreasing voltage. The increase that occurred in the number and size of the cavities when the voltage was decreased to 1.00 V can be seen in Fig.5.3 (b), to 0.05 V in Fig.5.3 (c) and to 0.02 V in Fig.5.3 (d) for scan rate of 2.00 mVs⁻¹. The pre-existing pores often promoted the formation of larger cavities as shown in the region marked in Figs.5.3 (b) and (c). New cavities were formed at a high rate and the graphite particle removal rate accelerated at voltages between 1.00 and 0.50 V. The area percentage of the damaged regions increased to 9.5% [Fig.5.3 (d)]. No further notable change occurred on the features of graphite surface at this magnification when the cycling continued. Another interesting observation can be made when Figs.5.3 (a)–(d) are considered together as it becomes apparent that a uniform contrast change took place on the entire graphite surface, i.e., the light tone of the initial surface became darker with the decrease of voltage. It was shown previously [9] that the development of this darker contrast was an indication of formation of a surface film (SEI) on the graphite surface due to electrolytic reduction.

For tests performed at 60°C, the initial microstructure of the sample used in the in-situ experiment is shown in Fig.5.3 (e) and was characterized by speckles indicating surface pores. As the voltage decreased in the first cycle to 1.00 V [Fig.5.3 (f)], 0.05 V [Fig.5.3 (g)], and 0.02 V [Fig.5.3 (h)], a slight increase in the number and area of the dark speckles occurred and some new cavities were formed. Overall, there was less damage on the graphite surface compared to that observed at 25°C. However, the contrast change of the graphite surface at 60°C was more pronounced [Fig.5.3 (h)]. The surface became much darker than that obtained at 25°C [Fig.5.3 (d)]. The enhanced contrast change could be attributed to the
faster development of a thicker SEI that provided uniform surface coverage at 60°C. These features of SEI were confirmed by detailed cross-sectional microstructural investigations (see Section 3.3). Thus, the SEI that formed at an elevated temperature appeared to have prevented graphite damage by reducing particle removal rate and cavity formation. The reduction in the initial capacity drop at 60°C reported in Fig.5.2 could be attributed to a reduction in the irreversible charge loss [30]. The irreversible loss was likely to be caused by the removal of particles from graphite surface and as there was less particle removal at 60°C the irreversible capacity loss was smaller.

Fig.5.4. (a) SEM image of the cross-sectional view of cavities formed on the graphite surface (Fig.5.3) as a result of fragmentation and delamination of graphite at 25°C. (b) Histogram showing the cavity size distribution on a graphite surface cycled at 25°C.

A typical example of the cavity formed at graphite surface at 25°C is shown in the cross-sectional microstructure in Fig.5.4 (a). Delaminated graphite layers have been marked inside one of the cavities. It has been previously suggested [10] that the coalescence of the delaminated layers could lead to graphite fragmentation that causes formation of these cavities. Presence of SEI was also noted inside the cavities. Using quantitative metallography, the area percentages of the damaged regions formed on the cycled graphite surface tested at two different temperatures were calculated. At 0.02 V, the average size of the cavities at 25°C
was 15.3±6.4 μm. A histogram showing the cavity size distribution is given in Fig.5.4 (b). Similar statistical analyses were conducted for each critical testing condition and mean cavity size is plotted in Fig.5.5 as a function of the voltage. For tests initiated from 3.00 V at 25°C and scanned at a rate of 2.00 mVs⁻¹, the percentage of cavities formed was negligible for voltages < 1.00 V. However, at 0.50 V, the area percent of the cavities formed on the surface increased abruptly to 9.5%. For lower voltages, the surface damage occurred at much slower rate. At 60°C, the rate of surface damage was the highest again between 1.00 and 0.50 V however the magnitude of damage was much less as only 2.8% of the graphite was removed. The reduction in the extent of particle loss at 60°C was attributed to the more effective protection provided by the SEI that was formed at that temperature. The morphology,

Fig.5.5. Plot showing calculated area percent of cavities formed on graphite surface in the first cycle at different temperatures. The arrows show no further change in area percentage until the end of the test (1500 s).
composition and microstructure of the SEI formed at 25 and 60°C are analyzed in the following sections.

5.3.3. Morphology of Graphite Surfaces with SEI

The SEM examinations of the surface and near surface (cross-sections) of the electrodes revealed that significant differences existed between the SEI morphologies that were formed at 25 and 60°C. The surfaces of the electrodes examined by SEM after testing for one cycle at 25°C consisted of an SEI layer unevenly distributed on the electrode surface as shown in Fig. 5.6 (a). The SEI appeared to have a patchy morphology consisting of

![Fig.5.6](image)

**Fig.5.6.** (a) SEM image showing the morphology of the SEI layer formed on graphite at 25°C after the first cycle. (b) Cross-sectional microstructure of the SEI formed at 25°C. The SEI is porous and non-uniform. The interface between the W-layer (deposited for protection against beam-induced damage) and the SEI is demarcated by a dotted line.
deposits of various heights. The cross-sectional morphology of the interface between graphite and the SEI is shown in Fig. 5.6 (b) where the SEI layer non-uniform and has a porous structure. The adhesion between the SEI and the graphite surface was poor in most places across the interface. The thickness of the layer was 415 ± 285 nm. In some locations, short segments of very thin (~20 nm) layers were observed. An example of such regions is marked in Fig. 5.6 (b). Several regions, 100-200 nm wide, located immediately below the deposits consisted of a lighter contrast that indicated possible diffusion of solvent to the graphite sub-surface.

Fig. 5.7. (a) SEM image showing the morphology of the SEI layer formed on graphite at 60°C after the first cycle. (b) Cross-sectional microstructure of the SEI formed at 60°C. The SEI is dense and uniformly covered the graphite surface.

The SEI layers that were formed on a graphite surface at an elevated temperature of 60°C were continuous and generally thicker [Fig. 5.7 (a)]. A typical secondary electron (SE)-
SEM image of the SEI/graphite cross-section is presented in Fig.5.7 (b). The average thickness of the layer was in the range of 435 ± 161 nm. SEI appeared to provide more uniform coverage than the one formed at 25°C. The layer was also dense as it was less porous. It was also noted that it was well adhered to the graphite surface and provided continuous bond to graphite along all sections investigated across the interface as shown in Fig.5.7 (b). In this case, solvent diffusion into the electrode subsurface was restricted. The difference in the SEI color contrast was caused by multiple ion-milling planes that were formed at variable depths.

![Fig.5.8. EDS elemental maps (with yellow indicating carbon, oxygen represented by red and chlorine by blue) depicting changes in graphite electrode surfaces after the first cycle (scan rate of 0.50 mVs⁻¹) at (a) 25°C and (b) 60°C.](image)

The EDS map of the graphite electrode surface obtained at 25°C, shown in Fig.5.8 (a), was noteworthy because it shows the distribution of the elements of interest, namely, carbon, oxygen and chlorine. These elements were identified as the possible constituents of the SEI since oxygen is a component of LiClO₄ (electrolyte salt) and/or Li₂CO₃ (formed during electrochemical reduction [6]). Presence of chlorine was indicative of the presence of residual LiClO₄ (electrolyte salt). The EDS map of the graphite electrode surface scanned at
60°C confirmed that the layers were rich in oxygen but not in chlorine [Fig.5.8 (b)]. Thus, the electrode surface was covered by a layer mainly consisting of carbon and oxygen that was indicative of the presence of Li$_2$CO$_3$. The lack of chlorine infers that the SEI formed at 60°C was deficient in residual LiClO$_4$.

5.3.4. Transmission Electron Microscopy of the SEI formed at 60°C

Detailed observations of the SEI/graphite interface generated during tests performed at 60°C were conducted at high magnifications and resolutions using TEM studies. A bright-field cross-sectional TEM image of the interface between the SEI layer and graphite is shown in Fig.5.9 (a). The TEM-based EDS elemental line-scanning data shown in this figure revealed the distribution profile of oxygen across the graphite/SEI interface. The concentration of chlorine was low. Fig.5.9 (b) is a high-resolution (HR)-TEM image of the SEI obtained from a region approximately 100 nm away from the interface. The HR-TEM image provides evidence for crystalline domains within an amorphous matrix. Specifically, crystalline domains of ~ 5-10 nm in size can be identified by the presence of regular lattice

![Fig.5.9. (a) Bright-field TEM image and EDS elemental line scans obtained from the SEI/graphite interface. (b) HR-TEM image showing crystalline domains of Li$_2$CO$_3$ and nano-fragments of graphite within the SEI.](image-url)
planes inside the regions marked by the dashed lines in Fig. 5.9 (b). These crystalline domains were identified either by (002) planes with interplanar spacings \( d \) of 0.28 nm that belonged to Li₂CO₃, or by (002) planes of graphite with \( d = 0.33 \) nm. The graphite fragments were likely detached from the electrode surface and mixed with the constituents of electrolyte reduction products in the SEI.

EELS analyses further confirmed that the SEI layer formed at 60°C was composed mainly of lithium, carbon and oxygen. Fig. 5.10 (a) shows the EELS spectrum that provides evidence for the presence of lithium (K-edge at 60 eV [31]). The oxygen K-edge at 534 eV [31,32] can be seen in Fig. 5.10 (b). The K-edge of carbon [Fig. 5.10 (b)] exhibited a fine structure composed of two peaks at 288 and 298 eV that were attributed to the formation of C=O and C-O bonds. The presence of lithium, oxygen and the C=O and C-O bonds indicated the presence of compounds like lithium alkoxides (R-OLi), lithium alkyl carbonates (RO-CO₂Li) and Li₂CO₃ in the SEI, in agreement with the EDS data.

![EELS spectra of (a) lithium, (b) carbon and oxygen in the SEI formed at 60°C.](image)

Fig. 5.10. EELS spectra of (a) lithium, (b) carbon and oxygen in the SEI formed at 60°C.
5.3.5. Compositional Analyses of SEI

Detailed analyses of the compositions of the constituents formed on graphite electrodes surfaces, cycled at 25 and 60°C, were conducted using XPS and FTIR. High-resolution XPS spectra that recorded the binding energies of C 1s are shown in Fig.5.11 (a) for the electrode cycled at 25°C. The binding energies obtained from the graphite surface

![High-resolution XPS spectra](image)

Fig.5.11. High-resolution XPS spectra (fitted Gaussian-shaped components) of graphite surface that recorded the binding energies of (a) C 1s after cycling at 25°C, (b) C 1s after cycling at 60°C, (c) Li 1s after cycling at 25°C, and (d) Li 1s after cycling at 60°C. The shift in the location of the Li-CO$_3$ group from 56.6 (at 25°C) to 55.4 eV (at 60°C) possibly occurred due to electrostatic charging of the SEI.
corresponded to peaks at 284.8 eV (C-C), 286.8 eV (C-O-C), 288.7 eV (O-C=O) and 290.2 eV (O-CO₂). The presence of O-CO₂, O-C=O and C-O-C groups suggested the formation of R-OLi and RO-CO₂Li [33] type of compounds in agreement with the EELS data [Fig.5.10 (b)]. These compounds are soluble in the electrolyte solvent and hence unstable [1,34]. The detection of the O-CO₂ group also inferred the presence of Li₂CO₃ within the SEI (as suggested by the EDS maps in Fig.5.8). In addition, the Li 1s XPS spectra in Fig.5.11 (b) show a peak at 56.6 eV that corresponded to the binding energy due to Li-CO₃. This provides further evidence that the SEI formed at 25°C contained Li₂CO₃. At 60°C, the locations of the binding energies for different groups in the C 1s high-resolution XPS spectra [Fig.5.11 (c)] were found to be similar to the ones seen in Fig.5.11 (a) although the peak intensities increased at high temperature. Particularly, the increase in the intensity of the O-CO₂ group was noteworthy. The Li 1s spectra obtained from the electrode cycled at 60°C [Fig.5.11 (d)] depicted a considerable increase in the Li-CO₃ peak intensity.

The post-cycling elemental surface composition presented in Table 5.1 showed that the chlorine content in the surface deposits decreased from 13.0 to 0.5 at.% . It also indicates an increase in concentration of lithium from 10.5 at.% at 25°C to 21.5 at.% at 60°C, and carbon from 23.5 at.% at 25°C to 40.4 at.% at 60°C, which again indicate the presence of higher proportion of Li₂CO₃ in the SEI compared to 25°C.

Table 5.1 – Peak comparative elemental composition analyses using XPS of graphite electrode surfaces in Fig.5.11.

<table>
<thead>
<tr>
<th>Temperature of Cell, °C</th>
<th>Elemental Composition of SEI (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li</td>
</tr>
<tr>
<td>25</td>
<td>10.5</td>
</tr>
<tr>
<td>60</td>
<td>21.5</td>
</tr>
</tbody>
</table>
Fig. 5.12. FTIR spectra obtained from graphite electrode surfaces tested at 25 and 60°C, and compared with reference spectra of Li$_2$CO$_3$ and LiClO$_4$.

The FTIR spectra obtained from the electrodes at 25 and 60°C are shown in Fig. 5.12 together with reference spectra of Li$_2$CO$_3$ and LiClO$_4$. The graphite surface cycled at 25°C exhibited intense vibrational bands at 1065, 1626, 2007, 3526 and 3567 cm$^{-1}$ that corresponded to absorptions at similar wavenumbers in the reference spectra of LiClO$_4$. 
Table 5.2 – Summary of compositional and microstructural analyses of the SEI formed at 25 and 60°C.

<table>
<thead>
<tr>
<th>Characterization Technique</th>
<th>Morphology and Composition of SEI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>SEM/FIB</td>
<td>• Non-uniformly distributed SEI on the graphite surface.</td>
</tr>
<tr>
<td></td>
<td>• SEI was unable to prevent graphite damage in the first cycle.</td>
</tr>
<tr>
<td>EDS</td>
<td>• Presence of elemental Cl in SEI.</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>• SEI microstructure consisted of crystalline domains of Li₂CO₃, Li₂O₂ and nano-sized graphite fragments.</td>
</tr>
<tr>
<td>EELS</td>
<td>• SEI contained Li, Cl, C-O and C=O groups that could be attributed to the presence of LiClO₄ and Li₂CO₃.</td>
</tr>
<tr>
<td>XPS</td>
<td>• Presence of O-CO₂, O-C=O and C-O-C groups in the C 1s XPS spectra suggested the formation of R-OLi and RO-CO₂Li. Detection of the O-CO₂ group also inferred the presence of Li₂CO₃ within the SEI.</td>
</tr>
<tr>
<td>FTIR</td>
<td>• Presence of residual LiClO₄ within the SEI was confirmed by vibrational bands at 1065, 1626, 2007, 3526 and 3567 cm⁻¹ that corresponded to absorptions at similar wavenumbers in the reference spectra of LiClO₄.</td>
</tr>
</tbody>
</table>

Consequently, evidence for the presence of residual LiClO₄ within the SEI formed at 25°C was confirmed. The FTIR spectra obtained after cycling the graphite surface at 60°C consisted of strong absorptions at 862, 1084, and 1423 cm⁻¹ and some weaker ones at 721,
2267, 2496 and 2958 cm$^{-1}$. These absorptions are in agreement with the previous XPS results and serve to confirm that the SEI layers formed at 60°C predominantly consisted of Li$_2$CO$_3$. Evidence for the presence of some residual LiClO$_4$ was found at high temperatures as well, as indicated by the occurrence of weak absorptions at 1626, 3526 and 3567 cm$^{-1}$. A summary of the compositional and microstructural observations described in Sections 3.3-3.5 is presented in Table 5.2.

5.4. Discussion

In Section 5.3.1, a drop in the planar capacity in the first cycle was reported (in Fig.5.2) to occur for both at 25°C and to a lesser extent at elevated temperatures (50 and 60°C). The capacity loss was accompanied by rapid cavity formation on graphite surface (Figs.5.3-5.5) that led to fragmentation [1,4,10], a phenomenon that has been described as electrochemical shock [35,36]. Once the SEI layer was formed, the electrode damage by cavitation was almost entirely prevented. Thus, the morphology of the SEI particularly its thickness and uniformity, as well as its composition, are all among the important factors that determine the planar capacity of graphite electrodes. Both the SEI morphology and composition changed significantly with the temperature as described in Sections 5.3.3-5.3.5. The following section (Section 5.4.1) considers the kinetics of Li-ion diffusion during SEI formation at different temperatures, and then examines the factors that influence SEI's functionality and the cyclic stability. These analyses led to the development of a new thermal treatment that increased battery's capacity (Section 5.4.2).

5.4.1. Variations in Li-ion Diffusion Kinetics with Temperature

The formation mechanisms and morphology of the SEI can be discussed in terms of the differences in the Li-ion diffusion kinetics, which in turn depend on the temperature ($T$)
and the voltage scan rate \( \left( \frac{dV}{dt} \right) \). The variations of current density \( \left( \frac{i}{A} \right) \), where \( A \) = electrode surface area) with the voltage \( (V) \) are shown in Fig.5.13 (a). These cyclic voltammetry scans were obtained at a constant \( \frac{dV}{dt} = 5.00 \text{ mVs}^{-1} \) for tests performed at three different temperatures of 25°C, 50°C and 60°C. Each scans revealed the formation of small peaks

![Fig.5.13. Plots of current density against voltage (vs. Li/Li⁺) obtained from cyclic voltammetry tests performed on graphite anodes between 3.00 V to 0.02 V (a) at different temperatures using a constant voltage scan rate of 5.00 mVs⁻¹, and (b) at a constant temperature of 60°C using different scan rates.](image)

(between 3.00 V and 0.02 V, as marked in Fig.5.13 (a)) that diminished with the increase in the test temperature. In general, similar voltage scan peaks are typically observed during the first cycle of potentiodynamic tests with graphite (vs. Li/Li⁺) and attributed to the reduction of EC. Their occurrence has been considered to coincide with the onset of SEI formation.
Table 5.3 – Peak voltage values observed during linear sweep voltammetry tests performed at different temperatures from \( V = 3.00 \text{ V} \rightarrow 0.02 \text{ V} \).

<table>
<thead>
<tr>
<th>Voltage scan rate ((dV/dt), \text{ mVs}^{-1})</th>
<th>25°C</th>
<th>50°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.57</td>
<td>0.68</td>
<td>0.79</td>
</tr>
<tr>
<td>2.00</td>
<td>0.47</td>
<td>0.64</td>
<td>0.69</td>
</tr>
<tr>
<td>5.00</td>
<td>0.43</td>
<td>0.50</td>
<td>0.56</td>
</tr>
</tbody>
</table>

The observed decrease in the intensity of voltage peaks with an increase in the cell temperature and scan rate can be attributed to the improved ionic conductivity of the electrolyte when the reaction kinetics becomes more facile [38,39]. It is useful to plot \( \frac{i_p}{A} \) against \( \frac{dV}{dt} \) in order to determine the changes in the Li-ion diffusion coefficient at different temperatures.

Table 5.4 – Peak current density values observed during linear sweep voltammetry tests performed at different voltage scan rates from \( V = 3.00 \text{ V} \rightarrow 0.02 \text{ V} \).

<table>
<thead>
<tr>
<th>Voltage scan rate ((dV/dt), \text{ mVs}^{-1})</th>
<th>25°C</th>
<th>50°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>4.18</td>
<td>2.84</td>
<td>4.63</td>
</tr>
<tr>
<td>2.00</td>
<td>8.34</td>
<td>16.32</td>
<td>11.10</td>
</tr>
<tr>
<td>5.00</td>
<td>16.88</td>
<td>24.11</td>
<td>26.76</td>
</tr>
</tbody>
</table>
temperatures. Using the Randles-Ševčík method [40,41] and the experimentally determined

\[ \frac{i_p}{A} \] values listed in Table 5.4, the following relationship could be established:

\[
i_p = 2.69 \times 10^5 n^2 C_{Li} \sqrt{D_{Li} \left( \frac{dV}{dt} \right)}
\]

(5.1)

where, \( n = 2 \) [1,42] is the number of electrons transferred during the SEI formation, \( C_{Li} = 106.4 \times 10^{-3} \) mol cm\(^{-3}\) is the concentration of LiClO\(_4\) in the electrolyte. The exposed electrode surface area, \( A = 19.625 \) mm\(^2\). Accordingly, the diffusion coefficient of Li-ion (\( D_{Li} \), cm\(^2\)s\(^{-1}\)) can be calculated from the slope of the linear relationship obtained by plotting \( \left( \frac{i_p}{A} \right) \) against

![Fig.5.14](image)

(a) Plot showing changes in the peak current density (\( i_p \)) with the square root of potential scanning rates (\( dV/dt \)). Li-ion diffusion coefficient (\( D_{Li} \)) was calculated from the slope. (b) Temperature dependence of \( D_{Li} \) at the electrode/electrolyte interface.
as in Fig.5.14 (a) with the slopes increasing with the operating temperature. The $D_{Li}^+$ values calculated from the slopes of lines in Fig.5.14 (a) for different temperatures are listed in Table 5.5. It is noted that the rate of Li-ion diffusion at the electrode/electrolyte interface increased with temperature, i.e., from $1.07 \times 10^{-8}$ cm$^2$s$^{-1}$ at 25°C to $3.25 \times 10^{-8}$ cm$^2$s$^{-1}$ at 60°C. The dependence of $D_{Li}^+$ to $T$ obeys an Arrhenius-type relationship as plotted in Fig.5.14 (b). Accordingly, the rate equation for Li-ion diffusion can be determined as a function of $T$ in the following form:

$$D_{Li}^+ = (7.26 \times 10^{-4})\exp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (5.2)

Table 5.5 – Diffusion coefficients of Li-ion ($D_{Li}^+$) at different temperatures obtained using the Randles-Ševčík method (Eq.5.1).

<table>
<thead>
<tr>
<th>Operating cell temperature, °C (K)</th>
<th>Diffusion coefficient of Li-ion ($D_{Li}^+$), cm$^2$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 (298)</td>
<td>$1.07 \times 10^{-8}$</td>
</tr>
<tr>
<td>50 (323)</td>
<td>$2.90 \times 10^{-8}$</td>
</tr>
<tr>
<td>60 (333)</td>
<td>$3.25 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

where, $R$ (= 8.314 JK$^{-1}$mol$^{-1}$) is the universal gas constant. From the slope of the log $D_{Li}^+$ vs. $T^{-1}$ plot shown in Fig.5.14 (b), the activation energy ($E_a$) of Li-ion diffusing at the SEI/graphite interface during SEI formation was calculated as 11.94 kJmol$^{-1}$ according to Eq.2. The enhancement of Li-ion diffusion rate at higher temperatures resulted in formation of an SEI that covered the whole graphite surface evenly, much more homogeneously than that at 25°C. The uniform SEI coverage (Fig.5.7) would serve to reduce the amount of graphite particle loss (Fig.5.4). Consequently, at 60°C, the planar capacity was high and the initial drop in planar capacity was lower compared to that at 25°C (Fig.5.2).
A schematic diagram illustrating the possible electrochemical reactions involved in the SEI formation on graphite at different temperatures is presented in Fig.5.15. During the decomposition of the electrolyte in the first cycle, EC is reduced by single electron transfer from the graphite surface to form $\text{CH}_2\text{OCO}_2^-$ [1]. With further electron transfer, $\text{CO}_3^{2-}$ is formed [Fig.5.15 (a)] and Li-ions from the electrolyte combined with the $\text{CO}_3^{2-}$ to form Li$_2$$\text{CO}_3$ in the SEI [Fig.5.15 (b)]. As previously indicated, at elevated temperatures R-OCO$_2$Li, R-OLi and semicarbonates may also convert to Li$_2$$\text{CO}_3$ that is stable at this temperature and has lower solubility in the battery electrolyte [16,43]. Apart from the role of an increase in the rate of Li$^+$ diffusion at the interface, it is also important to recall that the chemical reactions involved in the reduction of EC are also temperature dependent. As the driving force for the reduction reactions during SEI formation would increase with the cell temperature facilitating the dissociation of EC, the concentration of $\text{CO}_3^{2-}$ at the electrode/electrolyte interface is expected to increase [Fig.5.15 (c)]. It is conceivable that the enrichment of the interface by $\text{CO}_3^{2-}$ and a faster Li$^+$ diffusion at 50-60°C would promote the formation of an SEI with higher proportion of Li$_2$$\text{CO}_3$ [Fig.5.15 (d)]. The SEI formed at 60°C contained crystalline domains of Li$_2$$\text{CO}_3$ and nano-sized graphite fragments and these phases were stable at this high temperature [Fig.5.9 (b)]. These mechanisms are consistent with the experimental observations (Table 5.2), which revealed that the layer was rich in Li$_2$$\text{CO}_3$ at 60°C. An SEI enriched with Li$_2$$\text{CO}_3$ crystalline domains provides facile diffusion paths for Li$^+$ across the SEI as suggested in [44]. A uniform distribution of small Li$_2$$\text{CO}_3$ crystals may thus be the reason for the formation of a layer that is more homogeneous that formed at 25°C. The ease of Li$^+$ diffusion through the SEI would also mean higher planar capacity. However these points require further confirmation. In summary, the SEI that
Fig. 5.15. Schematic representation of the possible mechanisms of SEI formation at (a and b) 25°C and (c and d) 60°C. At 25°C, the slow rate of diffusion of Li-ions towards the interface led to the formation of a non-uniform SEI layer that was unable to protect the graphite surface from damage in the first cycle. A high diffusion rate at 60°C resulted in formation of a uniform SEI that could protect the graphite surface from damage.
forms at 60°C is stable and homogenously covers the graphite electrode thus acting as an effective protective layer.

5.4.2. Improvement of Capacity by Pre-Cycling at 60°C

According to the results in Section 3 and in the light of the above discussion, the differences in the morphology and composition of SEI should influence the capacity at different temperatures. It was suggested that faster Li⁺ diffusion at the electrode/electrolyte interface and a possibly high CO₃²⁻ concentration due to an accelerated dissociation of ethylene carbonate would lead to a Li₂CO₃-enriched SEI. It can be suggested that an SEI formed at 60°C would thus improve the subsequent cyclic performance at 25°C. To attest this hypothesis, graphite electrodes were cycled between 3.00 and 0.02 V at 25°C, with and without pre-cycling at 60°C (at a scan rate of 2.00 mVs⁻¹). The planar capacity of the electrode at 60°C was 3.11±0.12 mAh cm⁻² [Fig.5.16 (a)] and when the electrolyte temperature was decreased to 25°C after 10 cycles, the capacity abruptly dropped to 0.68±0.01 mAh cm⁻². However as Fig.5.16 (b) indicates, this was approximately 28% higher than the capacity of 0.53±0.03 mAh cm⁻² when graphite cycling was initiated at 25°C and continued at the same temperature. Thus a capacity increase was evident as a result of pre-cycling at 60°C.

It can also be suggested that when the graphite was cycled initially at 25°C, the capacity that will be subsequently attained at 60°C would not be as high if the test were started at this high temperature. An increase in the temperature to 60°C increased the capacity to 1.31±0.01 mAh cm⁻² following the initial electrochemical cycling at 25°C. This was about 60% lower than that observed when the cycling was initiated at 60°C without the initial cycling at 25°C. The SEI formed at 60°C being more efficient in protecting the
graphite surface, and possibly enhancing Li-ion diffusion more effectively than the one formed at 25°C, is the possible cause of this effect.

**Fig.5.16.** Variation of planar capacity with the cycle number during tests conducted at 25°C (a) with and (b) without a thermal pre-treatment at 60°C. The effects of further thermal cycling are also shown.

It is also important to confirm whether the SEI that forms at 60°C remains stable after cycling at different temperatures. The stability of the layer was tested by conducting alternating high and low temperature experiments and vice versa. Once the graphite is cycled at 60°C and cooled to 25°C and then cycled again at 60°C, an increase in the capacity to 2.99 mAh cm⁻² was observed that was comparable to the capacity observed during the first 10 cycles at 60°C [Fig.5.16 (a)]. After the 40th cycle, when the temperature was decreased once more to 25°C, the capacity dropped from 2.18 to 0.67 mAh cm⁻², which was again comparable to the capacity between the 10th and 30th cycle at 25°C. The capacity retention during such thermal cycling can be attributed to the stable and continuous SEI layer that was formed initially at 60°C.
In summary, the application of a thermal pre-treatment to electrodes in the 50-60°C range is shown to reduce the electro-mechanical degradation as well as enhance the cyclic performance of graphite electrodes operated at 25°C by almost 28%.

5.5. Conclusions

Graphite electrodes were subjected to linear sweep and cyclic voltammetry (vs. Li/Li+) using different voltage scan rates at 25, 50 and 60°C. The compositional changes in the solid electrolyte interphase (SEI) formed on graphite, including their microstructures and morphologies were investigated. The main conclusions are summarized as follows:

1. At 25°C, the planar capacity dropped by 40% in the first cycle and significant damage occurred on the graphite surface by graphite particle fragmentation and removal. In contrast, a 17% capacity drop was observed when cycling was conducted at 60°C. During the following cycles, a planar capacity of 3.11±0.12 mAhcm⁻² was attained at 60°C rather than 0.53±0.03 mAhcm⁻² at 25°C.

2. The SEI layer formed at 60°C predominantly consisted of Li₂CO₃ and was devoid of residual LiClO₄ identified at 25°C. The improved capacity at 60°C was attributed to the fast and uniform coverage of graphite electrode surface by the Li₂CO₃-enriched SEI.

3. Thermal pre-treatment of electrodes at 60°C reduced graphite degradation and enhanced the capacity of graphite electrodes at 25°C by 28%.

Bibliography


CHAPTER 6: Electrochemical Cycling Behaviour of Li₂CO₃ Pre-treated Graphite Anodes: SEI Formation and Graphite Damage Mechanisms

6.1. Introduction

Mechanical damage that occurs at the electrode surfaces causes lithium-ion batteries to suffer from a drastic capacity loss in the first cycle, a phenomenon that is sometimes referred to as electrochemical shock [1,2]. It was observed that the rate of capacity decrease was reduced when a solid electrolyte interphase (SEI) layer [3] would form and cover the electrode surface [4-6]. It was suggested that the SEI prevents further electrolyte decomposition by blocking transport of electrons while simultaneously allowing lithium-ions to pass through during charge-discharge cycles [7]. The relationship between SEI formation and graphite degradation by formation of surface cavities as a result of removal of fractured particles was observed during the first cycle using in situ microscopy [8] and solvent/Li⁺ intercalation-induced strain was measured using in situ Raman spectroscopy [9]. The growth of graphite cracks in subsequent cycles continues at a slower rate by Li⁺ insertion and/or solvent intercalation in the electrode surface and subsurface. The intercalation products, for example Li₂CO₃ and LiC₆, detected on the faces of cracks formed between graphite layers suggested that these deposits may reduce the cyclic stress intensity (the mechanical driving force) required for crack growth [10]. According to detailed SEM and cross-sectional TEM investigations, a well-adhered SEI with intertwined tubular morphology was found to provide uniform surface coverage and was effective in protecting the graphite anode rather than a rough SEI with columnar morphology that was non-uniform in thickness and less effective as a protective layer. This former type of SEI was formed during low scan rate tests (∼ 50 µVs⁻¹) and consisted of Li₂CO₃, Li₂O mixed with nano-sized graphite fragments [11].
Several studies suggested that the SEI was a mixture of organic species (e.g., ROCO₂Li and R-OLi) in the outer layer, close to the interface with electrolyte, and rich in inorganic components (e.g., Li₂CO₃ and Li₂O) in the inner part adjacent to the electrode interface [12-16]. The low solubility of the stable Li₂CO₃ in the electrolytic solution has been noted [13].

Improvements in the electrochemical performance were observed for electrodes whose surfaces were modified by various techniques [17-25]. A thermal pre-treatment of graphite electrodes conducted at 60°C produced a Li₂CO₃-enriched SEI that reduced graphite degradation and enhanced the capacity at 25°C by 28% [17]. Attempts to physically modify the morphology and chemistry of graphite surfaces included mechanical milling of natural graphite particles in O₂ and/or N₂ environments [18]. Other attempts to modify electrode surfaces encompass application of coatings such as carbon (thermal vapor decomposition treatment at 1000°C [19] or heat-treatment of graphite/PVC mixtures at 800-1000°C in Ar [20]), tin (autocatalytic deposition [21] and electrodeposition [22] techniques) and compounds such as polyacrylonitrile (PAN) [23] and polydimethylsiloxane (PDMS) [24]. Modification of the electrolyte by the application of film-forming additives such as vinyl ethylene carbonate (VEC) was suggested to assist in the formation of a stable passive electrode surface that could improve the cell performance [25]. In all these studies, it was commonly suggested that these additives modified the electro-active locations on the graphite surfaces and decreased the rate of solvent reduction during SEI formation; the SEI, formed in this way, improved the cyclic stability.

The hypothesis of this work is that the deposition of Li₂CO₃ particles on graphite surfaces prior to cycling would improve the SEI properties and increase the cyclic efficiency of graphite electrodes. The method used consisted of Li₂CO₃ deposition by means of
dissolution of particles in aqueous solutions, which may provide a facile technique especially for mass production of electrodes in practical applications. In order to assess the effectiveness of the deposition technique, detailed observations of the changes on the electrode surfaces in the time scale of the cycling process, along with compositional analyses of the modified surfaces, are required. The effects of deposition of Li\textsubscript{2}CO\textsubscript{3} particulates on the graphite surface were investigated to determine whether the battery’s irreversible charge loss and capacity retention would be positively affected by this treatment. The experimental methodology carried out for this purpose consisted of quantification of the graphite electrode damage during the first cycle by means of both in situ optical microscopy and in situ Raman spectroscopy. Prolonged cycling behaviour of Li\textsubscript{2}CO\textsubscript{3} pre-treated electrodes was investigated by studying the changes in the planar capacity. Surface and near-surface characterization techniques consisting of XPS, FTIR and high resolution TEM were used to determine the resulting changes in the composition of SEI formed on pre-treated electrode surfaces. The role of the SEI in protecting the graphite electrode surfaces from electrochemical damage and controlling Li\textsuperscript{+} and solvent co-intercalation were depicted.

6.2. Experimental

6.2.1. Description of Electrodes and Li\textsubscript{2}CO\textsubscript{3} Deposition Process

Electrodes were fabricated from high purity (99.999%) turbostratic graphite containing traces (~ 10 ppm) of Al, Fe, Mg and Si. The grain size of the graphite measured using cross-sectional TEM (JEOL 2010F STEM) was 25.7±10.9 nm. Detailed information about the microstructure and properties of the graphite used as the electrode material can be found in [11]. The graphite surfaces were treated with Li\textsubscript{2}CO\textsubscript{3} using a simple procedure. First, 100 ml aqueous solutions containing either 0.5 or 1.0 wt.% Li\textsubscript{2}CO\textsubscript{3} (with particle size
of 1.5 ± 0.5 μm) were prepared. To enhance the adhesion of the Li₂CO₃ particles to the graphite surface, small quantities (0.5 wt.%) of Agar, an inert polysaccharide extract obtained from seaweed, was added to the solution. When treated in < 0.5 wt.% Agar-containing aqueous solutions, the adhesion of Li₂CO₃ particles to graphite electrodes was unsatisfactory. On the other hand, aqueous solutions prepared with ~2.0 wt.% Agar were too viscous. Planar capacity changes of the untreated graphite electrodes (with number of electrochemical cycles) were compared with the electrodes pre-treated in 0.5 wt.% Agar-containing solutions, and it was observed that the presence of Agar did not have any significant impact on the test results. Hence, 0.5 wt.% Agar-containing aqueous solutions were used to provide enhanced adhesion between Li₂CO₃ particles and the graphite surfaces.

After complete dissolution of the Li₂CO₃ particles, graphite electrodes (with a diameter of 5 mm) were placed vertically inside the solution for 24 hours. The electrodes were then removed from the solution, dried in a furnace at 80°C for 3 hours and stored in vacuum.

6.2.2. Cell Assembly and Voltammetry Tests

The electrodes pre-treated with Li₂CO₃ were placed at the center of electrochemical cells constructed from polytetrafluoroethylene (PTFE). The cells were assembled and sealed in an Ar-filled MBraun LABstar workstation in which H₂O and O₂ levels were maintained below 1 ppm. A 99.99% pure lithium wire with a resistivity of 9.446 μΩ·cm (at 20°C) was used as the counter electrode. The reference electrode was also made of 99.99% pure lithium wire. The electrolyte solution consisted of 1 M LiClO₄ in a 1:1 (by vol.) mixture of ethylene carbonate (EC) and 1,2-dimethoxy ethane (DME). Linear sweep voltammetry (LSV) and
cyclic voltammetry (CV) tests were performed using a Potentiostat (Solartron Modulab System) operated between 3.00 and 0.02 V (vs. Li/Li⁺) using a scan rate of 2.0 mVs⁻¹.

6.2.3. Experimental Setup for in situ Optical Microscopy and micro-Raman Spectroscopy

For in situ observation of the changes in surface features during electrochemical cycling, the top surface of the graphite electrode, installed inside the cell, was placed directly under the (1000×) objective of a digital optical microscope with a depth of field 20 times

![Experimental setup for in situ Raman spectroscopy of surface changes on graphite anodes installed in an electrochemical cell with glass window. Only the top surface of graphite was exposed to the electrolyte. See [10] that shows a similar setup for in situ optical microscopy.](image)

Fig.6.1. Experimental setup for in situ Raman spectroscopy of surface changes on graphite anodes installed in an electrochemical cell with glass window. Only the top surface of graphite was exposed to the electrolyte. See [10] that shows a similar setup for in situ optical microscopy.
greater than that of a standard metallurgical optical microscope. In this way, microscopic features on the electrode surface that were as small as 5 μm could be detected in the time scale of the voltammetry experiments. The optical microscope was used interchangeably with a 50× objective of a Raman spectrometer during the voltammetry tests. A schematic diagram of the in situ experimental setup showing the Raman objective placed above the electrode can be seen in Fig.6.1. A 50 mW Nd-YAG solid state laser diode, emitting a continuous wave laser at the 532 nm excitation line, was used. The resulting Raman spectra were recorded using a Horiba spectrometer equipped with a CCD detector. The diameter of the laser spot on the specimen surface was 1 μm.

6.2.4. XPS and FTIR Analyses of Pre-treated Electrodes

XPS and FTIR were used to determine the composition of pre-treated graphite electrode surfaces before and after cycling. Kratos AXIS Ultra X-ray Photoelectron Spectrometer (XPS), that incorporates a magnetic immersion lens and a charge neutralization system with a spherical mirror analyzer, was used. Survey scans were carried out on an analysis area of 300×700 μm² using a pass energy of 160 eV. High-resolution analyses were performed on the same area with a pass energy of 20 eV. XPS could probe the electrode surfaces up to a depth of 7-10 nm.

Fourier transform infrared spectroscopy (FT-IR) of the pre-treated graphite electrode areas was performed using the attenuated total reflection objective on the IRScope II attached to a Bruker IFS-55. The diameter of the test area was 80-100 μm while the penetration depth of the IR beam was ~ 2 μm.
6.2.5. Transmission Electron Microscopy (TEM) of SEI

Cross-sectional TEM samples were excised on planes perpendicular to the SEI/graphite electrode interface using focused ion beam (FIB) inside a Zeiss NVISION 40 dual beam SEM/FIB. A 1 μm thick carbon layer was deposited on the selected areas where the cross-sectional trenches were made. A trench was milled normal to the SEI/graphite interface using Ga⁺ sputtered at an accelerating voltage of 30 kV and a beam current of 13.0 nA. The final milling of the cross-sectional sample was conducted using a low ion-beam current of 6.5 nA and a low voltage of 10 kV. The cross-sectional samples for the TEM investigations were milled from both sides to a thickness of 100 nm and removed using the FIB in situ “lift-out” technique. The samples were examined using an FEI Titan 80-300 HR-TEM operated at 80 kV to obtain high-resolution imaging and diffraction patterns of the SEI layers.

6.3. Results

6.3.1. In situ Observations of Changes in Morphological Features of Electrode Surface using Optical Microscopy

In situ observations of electrode surfaces were carried out at 1000× magnification during the LSV tests. Initially a high voltage of 3.00 V was applied and then the voltage was decreased at a constant scan rate of 2.00 mVs⁻¹ to a minimum of 0.02 V, i.e. \( V = 3.00 \text{ V} \rightarrow 0.02 \text{ V} \) (vs. Li/Li⁺) as shown in Fig.2 (a). For the untreated graphite, a reduction in current peak was observed when the voltage reached at 0.43 V as marked in the current density curve in Fig.6.2 (a). Similar current peaks were typically observed during the first cycle of potentiodynamic tests with graphite (vs. Li/Li⁺) and attributed to the reduction of EC [26,27]. Their occurrence can be considered to coincide with the onset of SEI formation.
Fig. 6.2. (a) Linear sweep voltammetry experiment performed using an untreated graphite electrode showing variation of current density between 3.00 and 0.02 V at a scan rate of 2.0 mV/s. Optical microstructures were obtained at 1000× showing (b) initial surface condition with some surface pores, and after (c) 1000 s, (d) 1250 s, (e) 1450 s, and (f) 1490 s. Slight overall contrast change indicates formation of SEI that was unable to prevent graphite surface damage. The arrow (国情) marks the same location (an initial pore) during successive phases of the experiment.
The purpose of in situ optical microscopy was to examine the efficacy of the SEI on the reduction of the electrode surface damage. When the untreated graphite electrode surface was examined prior to the initiation of the test, open pores appeared as dark speckles as can be seen in Fig.6.2 (b). These pores (formed during hot-pressing of the graphite) covered a small portion, 0.5±0.1%, of the electrode surface area and had diameters of 9-15 μm. During the voltage scan tests it was observed that 0.5-2.0 μm size graphite particles were removed from the surface and the locations, where particle removal occurred, were demarcated by dark spots on the optical microscopy images of the electrode surfaces. These damage features are referred here as cavities. The number and size of the cavities increased with decreasing the voltage. In some areas, cavities were formed from the initial pores but they were not always associated with the pre-existing pores. All cavities became enlarged when the voltage decreased to 1.00 V can be observed in Fig.6.2 (c), to 0.50 V in Fig.6.2 (d), to 0.10 V in Fig.6.2 (e) and to 0.02 V in Fig.6.2 (f). Consideration of the sequence of cavity formation and growth events in Figs.6.2 (b)-(f) revealed that the surface degradation rate increased notably below 0.50 V. Using quantitative metallography it was shown that the area percentage of cavities increased rather abruptly from 3.5±0.8% at 0.5 V [Fig.6.2 (d)] to 18.1±1.2% at 0.02 V [Fig.6.2 (f)]. No additional change could be observed at this magnification to suggest continuation of degradation on the graphite surface with further voltage cycling. However, it was observed that a uniform contrast change occurred on the entire graphite surface, i.e., the initial light tone of the surface became darker with the decrease of voltage Figs.6.2 (b)-(f). It was shown [8] that the development of this darker contrast was an indication of formation of a surface film (SEI) on the graphite surface due to electrolytic reduction.
Fig. 6.3. (a) Linear sweep voltammetry experiment performed using a pre-treated graphite electrode (1.0 wt.% Li$_2$CO$_3$) showing variation of current density between 3.00 and 0.02 V at a scan rate of 2.0 mV/s. Optical microstructures were obtained at 1000× showing the (b) initial condition, and after (c) 1000 s, (d) 1250 s, (e) 1450 s, and (f) 1490 s. The SEI could reduce graphite surface damage. The arrow (→) marks the same location (an initial pore) during successive phases of the experiment.

When the same LSV test, between 3.00 and 0.02 V, was performed on a pre-treated (1.0 wt.% Li$_2$CO$_3$) graphite surface, a current peak was observed at a voltage of 0.86 V [Fig. 6.3 (a)] i.e., at a higher voltage compared to 0.43 V as seen in Fig. 6.2 (a). The shift in the
appearance of the scan peak from 0.43 V (for untreated electrodes) to 0.86 V could be attributed to earlier initiation of SEI formation prompted by the pre-deposited Li$_2$CO$_3$ particles. The initial microstructure of the electrode is shown in Fig. 6.3 (b). As the voltage decreased to 1.00 V [Fig. 6.3 (c)], 0.50 V [Fig. 6.3 (d)], 0.10 V [Fig. 6.3 (e)], and 0.02 V [Fig. 6.3 (f)], only a slight increase in the number and surface area of the dark speckles occurred. The rate of surface damage was the highest at 0.50 V. The magnitude of damage was much less compared to the untreated graphite; area percentage of the graphite surface that exhibited damage in the form of cavities was limited to 5.3±0.2%. The SEI that formed on pre-treated graphite electrodes earlier during the test (i.e., at higher voltage) appeared to have reduced graphite degradation.

It is conceivable that the pre-treated electrodes prompted establishment of a uniform SEI that covered the graphite surface before significant degradation occurred. Evidence of uniform SEI coverage was found using XPS analyses that are discussed in Section 6.3.4. Also, the pre-treatment facilitated the formation of an SEI rich in crystalline Li$_2$CO$_3$ phase as observed by high resolution TEM and discussed in Section 6.3.5.

6.3.2. In situ Strain Measurement on Graphite Surface using Raman Spectroscopy

In situ micro-Raman spectroscopy was conducted in the time scale of CV experiments run from $V = 3.00 \, \text{V} \rightarrow 0.02 \, \text{V} (\text{vs. Li/Li}^+)$ at a constant scan rate of 2 mVs$^{-1}$, to record changes in the graphite surface characteristics. A series of Raman spectra recorded at 3.00 V, 1.00 V and 0.02 V (Fig. 6.4 (a)) showed the G-band (at 1581 cm$^{-1}$) of the untreated graphite electrode. The formation of this peak was attributed to the in-plane vibration of the $\sigma^*$-hybridized carbon atoms [30,31]. A shoulder peak at 1620 cm$^{-1}$ (D$'$) was also observed. In
**Fig. 6.4.** *In situ* Raman spectra obtained from (a) untreated and (b) pre-treated (1.0 wt.% Li$_2$CO$_3$) graphite electrodes when scanned from 3.00 $\rightarrow$ 0.02 $\rightarrow$ 3.00 V at a linear scan rate of 2.0 mVs$^{-1}$. (c) Plot showing changes in the position of the G-band observed in the Raman spectra obtained from untreated and pre-treated graphite electrode surfaces.
the literature, the formation of the D'-band was attributed to the asymmetry at the edges of
the graphite planes [31-33]. With the decrease in the voltage, the G-band shifted from 1581
cm$^{-1}$ (at 3.00 V) to 1589 cm$^{-1}$ (at 0.02 V). The frequency shift of the Raman band is related to
the uniaxial strain and the shear strain; the latter could be ignored due to its minor
contribution [34]. The relation between the Raman frequency and the strain could be
expressed as [34,35],

$$\frac{\Delta \omega}{\omega_o} = \gamma (\varepsilon_{xx} + \varepsilon_{yy})$$

(6.1)

where $\omega_o$ is the G-band frequency; $\Delta \omega$ is the shift in the frequency (from 1581 to 1589 cm$^{-1}$);
$\gamma=1.59$ is the Grüneisen parameter for graphite [36]; $\varepsilon_{xx}$ is the uniaxial strain, while $\varepsilon_{yy} \approx -0.2 \varepsilon_{xx}$ is the relative strain in the perpendicular direction according to the Poisson’s ratio of
graphite (=0.20). From these values, $\varepsilon_{xx}$ was calculated as $3.97 \times 10^{-3}$. During the reverse
sweep, the G-band shifted back and reached 1581 cm$^{-1}$ when the voltage was increased to
3.00 V. The shift in the location of the G-band was discussed in terms of the strain increase
in the graphite lattice [37,38]. It could be attributed to intercalation of solvent molecules. An
increase in the strain of 0.4% calculated from Eq.6.1 would be responsible for graphite
fragmentation and hence for the formation of cavities shown in Fig.6.2.

The spectra obtained from the surface of a pre-treated graphite electrode (1.0 wt.%
Li$_2$CO$_3$) are presented in Fig.6.4 (b). As seen in untreated electrodes, the D'-band was also
observed in the Raman spectra obtained from pre-treated graphite. However, the G-band
shifted only to 1583 cm$^{-1}$ at 0.02 V (from 1581 cm$^{-1}$ at 3.00 V). The changes in the location
of the G-band were plotted as a function of the time and voltage in Fig.6.4 (c). The smaller
change in the location of the G-band for pre-treated electrodes, compared to that observed in case of the untreated ones, could be attributed to a reduction in the strain (0.1%) in the graphite layers. In case of untreated graphite electrodes, the shift in the G-band was higher since the SEI was not as effective to reduce the diffusion of solvent molecules. On the other hand, SEI formed on the pre-deposited Li₂CO₃ particles could reduce co-intercalation that would decrease the strain in graphite and, hence, less damage would occur by cavity formation. The damage in the graphite structure contributed to the irreversible charge loss [39] and caused a drop in the capacity as described in Section 6.3.3.

6.3.3. Electrochemical Capacity of Electrodes during Prolonged Cycling

Untreated and pre-treated graphite electrodes were subjected to CV tests for 100 cycles (each experiment starting from V = 3.00 V → 0.02 V (vs. Li/Li⁺) at a constant scan rate of 2.00 mVs⁻¹). The purpose of these experiments was to evaluate the long-term cycling performance of Li⁺ battery electrodes in order assess whether the Li₂CO₃ pre-treatment would improve electrochemical cycling stability of the electrodes. The planar capacity was calculated from the area under the current density (mAcm⁻²) and time (hours) curves for each cycle and plotted in Fig.6.5 as a function of the number of cycles. For untreated graphite electrodes, the planar capacity rapidly dropped from 0.81 mAh cm⁻² in the first cycle to 0.48 mAh cm⁻² in the second cycle, i.e., a decrease of ~40%. In case of graphite electrodes pre-treated in aqueous solutions containing 0.5 wt.% Li₂CO₃, the capacity drop between the first (1.19 mAh cm⁻²) and second (1.10 mAh cm⁻²) cycles was 7.5%. The first cycle capacity for graphite electrodes pre-treated in 1.0 wt.% Li₂CO₃-containing aqueous solutions was 0.96 mAh cm⁻² and the capacity dropped to 0.93 mAh cm⁻² in the second cycle resulting in only a
3% drop. Thus, the pre-treatment procedure considerably decreased the extent of irreversible charge consumption during the SEI formation in the first cycle. At the completion of 100 cycles, the capacity dropped to 0.54 mAh cm\(^{-2}\) that was significantly higher than that observed in case of untreated graphite electrodes (0.11 mAh cm\(^{-2}\)).

In summary, Fig.6.5 indicates that the capacity retention during initial as well as long-term cycling improved for graphite electrodes that contained Li\(_2\)CO\(_3\) particles prior to cycling. Improved planar capacity was possibly due to enhanced Li\(^+\) diffusion through the SEI formed on pre-treated surfaces. The details of the possible mechanisms of Li\(^+\) diffusion through the SEI formed on pre-treated electrodes are discussed in Section 6.4. The
composition of the SEI that shed light on these mechanisms is analyzed in the following section.

6.3.4. Characterization of SEI using XPS and FTIR

High-resolution XPS spectra of the pre-treated (1.0 wt.% Li$_2$CO$_3$) graphite surface is shown in Fig.6.6 (a) and depicts binding energies of the fitted Gaussian-shaped components of C 1s located at 284.5 eV (C=C), 285.65 eV (C-C), 287.35 eV (C-O-C), 288.75 eV (C=O) and 289.65 (O-C=O). The detection of C-O-C, C=O and O-C=O groups are indicative of the presence of Li$_2$CO$_3$ on graphite surface prior to cycling. The Li$_2$CO$_3$ did not cover the surface uniformly, thus prominent C=C peaks from the exposed graphite are evident in Fig.6.6 (a).
Fig. 6.6. High-resolution XPS spectra showing the binding energies of C 1s obtained before cycling from (a) pre-treated graphite surface (1.0 wt.% Li$_2$CO$_3$), and after cycling of (b) untreated and (c) pre-treated (1.0 wt.% Li$_2$CO$_3$) graphite surfaces.
The spectra obtained from an untreated graphite surface after 10 cycles, shown in Fig.6.6 (b), revealed that the while C=C peak disappeared, peaks corresponding to the binding energies of C 1s at 284.7 eV (C-C), 286.2 eV (C-O-C), 288.7 eV (O-C=O) were still present and a new peak at 290.4 eV (CO$_3^{2-}$) appeared suggesting the formation of lithium alkoxides (R-OLi), lithium alkyl carbonates (R-OCO$_2$Li) and Li$_2$CO$_3$. These compounds are expected to form on the cycled graphite electrode surface as a result of electrolyte solvent reduction [13].

Fig.6.6 (c) shows the spectra obtained from a pre-treated (1.0 wt.% Li$_2$CO$_3$) graphite surface after cycling and consisted of peaks at similar binding energies as seen in Fig.6.6 (c) but having higher intensities. Particularly, the increased intensity of the CO$_3^{2-}$ peak at 290.4 eV provides evidence that the concentration of Li$_2$CO$_3$ in the SEI formed on pre-treated electrodes was higher. Being a stable compound, the pre-deposited Li$_2$CO$_3$ particles are not expected to react with the other SEI components like R-OCO$_2$Li, R-OLi, etc. [12-16]. It should be noted that XPS could penetrate up to a depth of 7-10 nm. The C=C group did not appear after cycling on either untreated [Fig.6.6 (b)] or pre-treated [Fig.6.6 (c)] electrodes unlike the initial spectra in Fig.6.6 (a), because graphite surfaces were covered by the SEI after the first cycle.

Table 6.1 – Peak comparative elemental composition analyses using XPS of graphite electrode surfaces in Fig.6.6. Graphite electrodes were pre-treated in 1.0 wt.% Li$_2$CO$_3$-containing aqueous solution.

<table>
<thead>
<tr>
<th>Condition of graphite surface</th>
<th>Elemental Composition of Electrode Surface (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li</td>
</tr>
<tr>
<td>Before cycling (pre-treated)</td>
<td>3.4</td>
</tr>
<tr>
<td>After cycling (pre-treated)</td>
<td>18.3</td>
</tr>
<tr>
<td>After cycling (untreated)</td>
<td>10.5</td>
</tr>
</tbody>
</table>
The post-cycling high-resolution XPS compositional analyses, carried out on an electrode area of 300×700 μm², are presented in Table 6.1. The decrease in the carbon concentration from the initial 70.7 at.% to 23.5 at.% for the untreated graphite surfaces, and to 17.6 at.% for pre-treated surfaces was again attributed to the SEI coverage of graphite. The analyses revealed the lithium concentration of pre-treated graphite electrode surfaces increased from 3.4 at.% (before cycling) to 18.3 at.% after 10 cycles. At the same number of cycles, lithium concentration increased to 10.5 at.% on the untreated surfaces. Also, the post-cycling oxygen concentrations of pre-treated (52.9 at.%) and untreated (52.2 at.%) graphite surfaces were both higher than the initial oxygen content of 22.0 at.%. The higher increase in the lithium and oxygen concentrations in the SEI formed on the pre-treated electrodes suggests that the SEI contained a greater proportion of R-OLi, RO-CO₂Li and Li₂CO₃. The FTIR results presented in the following paragraph provided further evidence for the presence of Li₂CO₃ and residual LiClO₄ in the SEI.

The FTIR plot in Fig.6.7 (a), obtained from a pre-treated graphite surface (1.0 wt.% Li₂CO₃) confirmed the presence of Li₂CO₃ by identifying the absorptions at 1801, 1423, 1084 and 862 cm⁻¹. Fig.6.7 (b) shows FTIR spectra obtained from cycled graphite electrode surfaces in comparison with the reference spectra of Li₂CO₃ and LiClO₄. The spectrum obtained from the surface of an untreated graphite electrode after 10 cycles consisted of absorptions at 3566, 3527, 2009 and 1625 cm⁻¹ that occur due to presence of residual LiClO₄. Additionally, the absorption at 1084 cm⁻¹ was due to the presence of Li₂CO₃ formed during the electrolytic reduction of EC [40].
Fig. 6.7. FTIR spectra measured from pre-treated graphite electrode surfaces (1.0 wt.% Li₂CO₃) (a) before cycling and compared with the reference spectra of Li₂CO₃; (b) after cycling and compared with spectra obtained from untreated graphite electrode surfaces, Li₂CO₃ and LiClO₄.
For the pre-treated graphite electrode surfaces (1.0 wt.% Li$_2$CO$_3$), strong absorptions were found at 1423, 1084 and 862 cm$^{-1}$ that were readily attributed to the formation of an SEI with higher Li$_2$CO$_3$ concentration. The absorption at 1084 cm$^{-1}$ arising from the presence of Li$_2$CO$_3$ was slightly intensified after EC reduction. In addition, the SEI also contained residual LiClO$_4$ that was indicated by the absorptions at 3566, 3527, 2009 and 1625 cm$^{-1}$. Both XPS and FTIR characterization techniques allowed scanning of large electrode surface areas and thus evidence for Li$_2$CO$_3$ enhancement of SEI that was formed on pre-treated graphite electrodes was well supported. The microstructures of the SEI formed on graphite electrodes, with and without pre-treatment, were analyzed subsequently and the results are given in Section 6.3.5.

6.3.5. High Resolution TEM Analyses of SEI

The TEM images of SEI formed on Li$_2$CO$_3$-treated surfaces consisted of nanocrystalline domains dispersed in an amorphous matrix. Li$_2$CO$_3$ nano-crystals of size 14.6±6.9 nm can be identified in a typical TEM image in Fig.6.8 (a). These crystals were randomly dispersed in an amorphous matrix (consisting of Li, O, and C [17]), and concentrated near the SEI/electrolyte interface. A fraction of these crystals could have also formed during EC reduction and SEI formation. Electron diffraction patterns obtained from the SEI [Fig.6.8 (b)] showed rings of diffraction spots that revealed the presence of crystallographic planes with $d$-spacings of 0.42 nm and 0.29 nm, corresponding to the \{110\} and \{202\} planes of Li$_2$CO$_3$ [41], respectively. Weak diffraction ring patterns matching to $d$-spacings of 0.21 nm and 0.16 nm were also identified in the SEI, which were consistent with \{100\} and \{004\} planes of graphite [42]. This observation suggested that the graphite particles were removed from the electrode surfaces during cycling (previously seen in Fig.6.3) and mixed with the
Fig. 6.8. (a) High-resolution TEM image of the SEI formed on Li$_2$CO$_3$-treated graphite electrode showing the existence of randomly-oriented Li$_2$CO$_3$ crystals of size 14.6±6.9 nm. (b) An electron diffraction pattern obtained from a region (diameter = 60 nm) within the SEI layer shows diffraction rings with strong intensity corresponding to crystallographic planes of Li$_2$CO$_3$, along with weaker rings of graphite planes indicating the presence of graphite fragments.
Fig. 6.9. High-resolution TEM images of (a) the SEI formed on Li₂CO₃-treated graphite and (b) untreated graphite electrodes. FFT-derived diffraction pattern (inset) of a marked crystalline domain suggested the presence of Li₂CO₃ and graphite fragments within the SEI formed on untreated electrodes.

SEI. TEM images taken from the pre-treated graphite surfaces [Fig.6.9 (a)] indicated that the microstructure of SEI exhibited crystals with planes belonging to Li₂CO₃ but not to the graphite. In contrast, the SEI formed on the untreated electrodes exhibited crystalline regions with diffractions arising from both Li₂CO₃ and graphite [Fig.6.9 (b)].
6.4. Discussion: Role of the Pre-treatment on Improving Cyclic Performance

Based on the microstructural and spectroscopical evidence, a depiction of the possible mechanisms responsible for SEI formation on the pre-treated and untreated graphite surfaces are schematically shown in Figs.6.10 (a)-(d).

![Fig.6.10. Schematic representation of the mechanisms of SEI formation and Li\(^+\) diffusion. (a) The SEI formed on untreated graphite surfaces was unable to prevent damage by graphite fragmentation and crack growth, causing formation of large number of cavities. (b) After prolonged cycling, the capacity of Li\(^+\) cells with untreated graphite electrodes dropped considerably due to reduction of Li\(^+\) diffusion through the SEI. (c) The SEI layer formed in presence of Li\(_2\)CO\(_3\) particles, deposited on graphite surface prior to cycling, reduced electrode damage in the first cycle; (d) the SEI, with higher Li\(_2\)CO\(_3\) concentration, assisted in enhancing stability and Li\(^+\) diffusion that improved the capacity retention.](image)

The insertion of solvent molecules [43-45] into the graphite surfaces was suggested to be responsible for the fracture and loss of the near surface graphite particles [Fig.6.10 (a)]. For example, Li\(^+\) solvated with organic solvent molecules were proposed to intercalate into
the graphite lattice [43] and cause lattice defects [44]. The damage inflicted to the untreated graphite surface was highest particularly during the first cycle resulting in the formation of a large number of surface defects in the form of cavities as observed in Figs.6.2 (b)-(g) and schematically shown in Fig.6.10 (a). An irreversible and large drop in capacity is recorded after the first cycle.

As discussed in the literature [4,5,8], the formation of the SEI slows down the rate of electrode surface damage and the rate of decrease in capacity becomes less in the subsequent cycles (Fig.6.5). For a particular type of graphite, the extent of this second drop in capacity is then determined by the chemical composition of the SEI as well as the thermal stability of the SEI [17] as these factors would affect the ionic diffusion rates. An SEI that provides uniform coverage would suppress the occurrence of further damage in the form of crack growth [11]. Similarly, an SEI that reduces the mechanical damage, without negatively effecting Li$^+$ diffusion during prolonged cycling, is desirable [Fig.6.10 (b)]. In the current experiments that used untreated graphite electrodes, a 77% drop in capacity was recorded after 100 cycles.

Pre-deposition of Li$_2$CO$_3$ particulates on graphite surfaces affected both the first cycle performance and the long-term stability positively. It can be argued that during the first cycle of the CV tests, as the pre-deposition of Li$_2$CO$_3$ resulted in the earlier formation of SEI, i.e, at a higher voltage (Fig.6.3 (a)), the SEI was more effective to reduce the graphite damage (Figs.6.3 (b)-(g)) as summarized in Fig.6.10 (c). In addition, the SEI was richer in Li$_2$CO$_3$ (Figs.6.7 (b) and 6.8 (a)). The high concentration of Li$_2$CO$_3$ crystals could facilitate Li$^+$ diffusion and, consequently, provide the long-term cycling stability [Fig.6.10 (d)]. These mechanisms are discussed in detail in the following paragraphs.
As noted in Section 6.3.2, the intercalation of solvent molecules would produce a strain of 0.4% in the graphite lattice that caused a shift in the location of the Raman G-band (Fig.6.4). The tensile stress exerted at this strain could be sufficiently high to cause fracture of graphite layers. From the atomistic point of view, the intercalated solvent molecules could act as barriers to the motion of dislocations at the basal planes of turbostatic graphite leading to nucleation of micro-cracks [46-48]. In the pre-treated electrodes, the Raman shift was negligible and so was the strain due to intercalation (0.1%), consistent with smaller amount of graphite damage. The consequence of fragmentation-induced cavity formation is a sharp capacity drop in the first cycle (Fig.6.5). With less damage in the pre-treated electrodes, the first cycle capacity drop was only 3% compared to 40% for the untreated electrodes.

The SEI formed on pre-treated graphite surfaces predominantly consisted of Li$_2$CO$_3$ (Figs.6.7 and 6.8). When considering the role of the pre-treatment on the stability of the SEI layers, attention should be given to the fact that Li$_2$CO$_3$ is almost insoluble in the solvent [13]. The pre-deposited particles may have acted as heterogeneous nucleation sites and expedited Li$_2$CO$_3$ formation during the electrochemical reduction of EC. Once the Li$_2$CO$_3$-enriched SEI was formed, it is conceivable that the solvent diffusion pathways would have become blocked. This might be a possible mechanism by which the SEI could reduce electrode surface damage (Fig.6.3) and prompted enhanced Li$^+$ diffusion during prolonged cycling.

The exact mechanisms for Li$^+$ diffusion through the SEI layer are not known. Recent studies reported that certain crystallographic planes of Li$_2$CO$_3$ could facilitate Li$^+$ diffusion [49,50]. The Li$_2$CO$_3$ crystals shown in Fig.6.8 (a) may provide favourable pathways for Li$^+$ diffusion through the SEI and to reach the graphite electrode surface. Consequently,
it can be suggested that the SEI facilitated Li\(^+\) diffusion that enabled capacity retention during long-term cycling (i.e., up to 100 cycles, Fig.6.5).

In summary, the Li\(_2\)CO\(_3\) enrichment of SEI as a result of the pre-treatment was beneficial to reducing solvent co-intercalation in the first cycle and less damage at the electrode surface occurred. During prolonged cycling, the Li\(_2\)CO\(_3\) enriched-SEI remained stable and promoted Li\(^+\) diffusion that helped to retain the battery capacity.

6.5. Conclusions

Graphite electrode surfaces were treated in aqueous solutions containing 0.5 and 1.0 wt.% Li\(_2\)CO\(_3\) particles and subjected to CV tests. The effects of the Li\(_2\)CO\(_3\) pretreatment on the SEI’s microstructure and morphology were examined. The composition of the SEI was characterized using XPS and FTIR, and details of the phases formed with the SEI were studied using high resolution TEM. The graphite surface and subsurface damage mechanisms were determined by in situ optical microscopy and Raman spectroscopy. The main conclusions arising from these investigations are as follows:

1. In the first cycle, the SEI was formed earlier (at a higher voltage) on the Li\(_2\)CO\(_3\) pre-treated graphite surfaces compared to the untreated graphite electrode, and served to decrease the intensity of electrode degradation that occurred by fracture and removal of graphite particles with the beneficial consequence of reducing the irreversible capacity drop.

2. After 100 CV cycles, the pre-treated graphite electrodes retained most of their planar capacity at 0.54 mAh cm\(^{-2}\) in contrast to the untreated electrodes that recorded a drastic decrease to 0.11 mAh cm\(^{-2}\). It was proposed that the Li\(_2\)CO\(_3\) enriched SEI
helped to improve the retention of the planar capacity during long-term cycling by facilitating Li$^+$ diffusion.

In summary, pre-treatment of Li$^+$ battery electrodes using Li$_2$CO$_3$ containing aqueous solutions provides a convenient and effective way to reduce electrode damage and improve long-term cycling capacity.

Bibliography


CHAPTER 7: Capacity Fading Mechanisms of a Sn-Carbon Fibre Composite Anode Cycled in Lithium-ion Cells

7.1. Introduction

Graphite is the commonly used anode material in rechargeable Li-ion batteries [1,2], where the intercalation of Li-ions between the graphene layers lead to the formation of LiC_x compounds. The maximum theoretical capacity of graphite is 372 mAh g⁻¹ [3] that corresponds to the formation of LiC_6. Graphite surface damage by fragmentation into graphite particles of 5-10 μm size is the most intense during the first cycle [4]. Once the solid electrolyte interphase (SEI) layer [5] forms, the intensity of graphite degradation decreases [4]. In a recent study [6], a uniform and continuous SEI with a tubular morphology that was formed during low scan rate tests (0.05 mVs⁻¹) was effective in lessening graphite damage. Yet, delamination of graphite layers by the formation of interlayer cracks adjacent to SEI/graphite interfaces [7] could lead to a gradual decline of capacity. In another study, a pre-treatment conducted at 60°C generated a Li_2CO_3-enriched SEI that ensued a 28% increase in battery capacity at 25°C [8].

The limited capacity of graphitic anodes and their severe structural disordering upon prolonged charge-discharge cycling in Li-ion batteries [9] have attracted an interest in metals (e.g., Si, Sn, Sb, In, Bi, Al) as alternative anode materials [10]. Sn and its oxide-based compounds are particularly important because of their high theoretical capacity of 992 mAhg⁻¹ [11]. Li-ion insertion in Sn-based anodes may lead to the formation of a range of Li-Sn intermetallics [12]. However, large volume changes of electrodes made of pure Sn (in the order of 300%) that occur during charge-discharge cycling of the Li-ion cells, cause rapid fragmentation of Sn [11,12], resulting in less than 50% capacity retention after only ten
cycles [12-14]. In order to alleviate the shortcomings of the pure Sn anodes, one of the main strategies implemented is to develop anodes consisting of Sn-based intermetallics and composites, and anodes with micro- and nano-scale surface textures. In Sn-based intermetallic anodes such as Cu<sub>6</sub>Sn<sub>5</sub> [15-17], CoSn<sub>3</sub> [18] and Ni<sub>3</sub>Sn<sub>4</sub> [19-21], it has been suggested that Cu, Co or Ni form an inactive matrix that acts as a buffer to volume changes due to Li<sub>x</sub>Sn formation subsequently. This leads to lower specific capacities (e.g., from 500 mAh g<sup>-1</sup> to 200 mAh g<sup>-1</sup>) but significantly higher capacity retentions (e.g., from 20% to 80% after forty cycles), compared to anodes containing pure Sn [16]. Another strategy used to improve the capacity retention is the development of multiphase composite anodes consisting of a mixture of Sn and oxides [22] or carbonaceous materials [23-25]. Similar to the intermetallic anodes, the second phase in the Sn-based composite anodes accommodates the cycling-induced volume changes. Some of these composite anodes have shown high reversible capacity and good capacity retention, but the multi-step processes used to produce these materials are generally more complicated than those used in industry [26].

Anodes with micro- and nano-scale surface textures provide a large surface-to-volume ratio that improves the tolerance for the volume change, the chemical reactivity with the electrolyte, and the electronic contact with the current collector [27-29]. For these reasons, the use of metallic foams [30-32], nanopillar-textured Cu surfaces [33] and carbon fibre paper (CFP) [34] as current collectors for Sn-based anodes have shown to improve the cycling performance of anodes in rechargeable Li-ion cells. In particular, CFP is a lightweight material with a large surface area and good electrical conductivity. As such, it can be used as a substrate on which Sn coatings can be electrodeposited. This manufacturing method may offer the potential of producing uniform metallic coatings with controlled microstructures and morphologies [35,36]. Furthermore, CFP can be used as both the current collector and
an active component in the electrode construction, enhancing the specific capacity of the electrode, compared to an electrode constructed based on an inactive current collector.

Combining these strategies may provide new electrode designs for the next generation of high-performance Li-ion batteries. In an attempt to assess these assumptions, we reported the electrochemical performance of a new Sn-carbon fibre composite anode (Sn-CFP) in a recent study [37], fabricated by electrodepositing a Sn coating on a CFP sheet. The coating had an ultrafine grain structure that was expected to benefit the cycling performance by reducing crack size and delamination from the current collector during charge-discharge cycles [11]. The enhanced performance of the Sn-CFP anode was attributed to the small thickness and large surface area of the Sn coating covering the carbon fibres, as well as the double role played by carbon fibres as current collector and active material. Sn-CFP electrodes depict higher capacity compared to graphitic anodes. Degradation of the Sn coating leads to a gradual drop in the capacity and this has to be addressed for these anodes to be used in rechargeable Li-ion batteries.

The above survey shows that understanding of the micromechanisms responsible for the electrochemical processes and degradation in the Sn-CFP electrodes is essential for designing robust Sn-carbon composite anodes with prolonged cycling performances. Consequently, the aim of this study is to investigate microscopical changes that take place in the cycled Sn-CFP anodes as they relate to the electrochemical performance of the Li-ion cells.
7.2. Experimental

7.2.1. Description of Materials Used

Anodes were fabricated from randomly-oriented 7.5±1.5 μm diameter fibres of a 0.37 mm thick Toray CFP sheet with a porosity of 78%. The Toray CFP sheet consists of PAN carbon fibers with a tensile strength of 24 MPa, the flexural modulus being 10 GPa. Sn-coated CFP electrodes were fabricated by electrodepositing an Sn coating with a mass loading of 3.2±0.2 mg cm⁻² on the carbon fibres. A detailed description of the electrodes’ preparation is presented elsewhere [37]. This process produced a tin coating with an ultrafine grain size. The carbon fibres, examined prior to coating, are shown in Fig.7.1 (a). Fig.7.1 (b)

Fig.7.1. (a) SEM image of carbon fibres before coating; (b) high magnification SEM image of the region marked as (b) in (a) showing the fibre’s surface texture; (c) SEM image of Sn-coated fibres; (d) high magnification SEM image of the equi-axed Sn grains present in the region marked as (d) in (c).
is a high magnification SEM image obtained from a region marked as (b) in Fig.1 (a). The fibre surface consisted of lamellar-type structures stacked parallel to the fiber axis with longitudinally and laterally interlinked layer planes. Fig.7.1 (c) shows the coated fibres that were uniformly covered with Sn, and a high magnification image of the Sn grains, obtained from a region marked as (d) in Fig.7.1 (c), is shown in Fig.7.1 (d). The Sn grains were nearly equi-axed with an average size of 350±50 nm.

A bright field cross-sectional scanning STEM image of a single layer of Sn grains across the thickness of the as-prepared coating has been shown in Fig.7.2 (a). It can be seen that the coating had good adhesion to the CFP substrate. The Sn coating on the carbon fibres had a thickness of 500±100 nm. This was the average thickness of the coating in the coated side of the CFP, i.e., the top 65±5 μm of the total 370 μm CFP’s thickness. A high-resolution (HR) TEM image obtained from a location adjacent to the carbon fibre interface marked as (b) in Fig.7.2 (a) is shown in Fig.7.2 (b). The Sn/carbon fibre interface was mostly continuous. The d-spacing measured for Sn was 0.29 nm that corresponded to the (200) planes, whereas the interplanar spacing of the fibre was 0.34 nm corresponding to the (002) planes of carbon.

7.2.2. Description of Galvanostatic Tests

Galvanostatic charge-discharge cycling tests, with a voltage cut off window of 0.02-1.50 V vs. Li/Li⁺, were conducted on CFP and Sn-CFP electrodes in Li-ion cells by means of a Potentiostat (Solartron Modulab System) operated using current densities of 0.75 mA cm⁻² and 1.50 mA cm⁻², respectively. The electrodes (anodes) were placed inside a CR2032-type coin cell with a Li counter electrode, a polypropylene membrane (Celgard 2400)
Fig. 7.2. (a) Cross-sectional STEM image of a single layer of Sn grains across the coating thickness; (b) HR-TEM image obtained from a location (marked as (b) in (a)) at the fibre/Sn interface.
separator and an electrolyte composed of 1 M LiPF$_6$ in a mixture of ethylene carbonate (EC),
dimethyl carbonate and diethylene carbonate (1:1:1 by vol.). Li-ion cells were assembled and
sealed in an Ar-filled MBraun LABstar workstation, where H$_2$O and O$_2$ levels maintained
below 1 ppm.

7.2.3. SEM and TEM Investigations of Coated and Uncoated CFP

An FEI Quanta 200 FEG scanning electron microscope (SEM) equipped with an
EDAX energy dispersive X-ray spectrometer (EDS) and an extreme high-resolution (XHR)-
SEM, FEI Magellan 400 with sub-nanometer resolution, was used to study the surface
morphologies and compositions of both the coated and uncoated electrodes before and after
the galvanostatic cycling. EDS maps of the composite electrodes’ surfaces for C and Sn were
acquired using a voltage of 15 kV and sixteen scanning frames were used for each
measurement.

In addition, detailed transmission electron microscopy (TEM) studies were carried
out on the Sn-CFP electrodes, in the as-prepared condition and after the electrochemical
experiments using cross-sections excised using focused ion beam (FIB) milling. Similar TEM
investigations were conducted on the uncoated CFP electrode for comparison. A Zeiss
NVision 40 dual beam SEM/FIB instrument was employed to mill trenches on the carbon
fibres, using Ga ion beam currents ranging from 13 nA to 700 pA at a voltage of 30 kV. In
this way, cross-sectional TEM samples were prepared in a direction parallel to the fibers’
diameter. These samples were sectioned and removed from their original locations through a
technique referred to as “lift-out” FIB technique. First, a trench was ion-milled on each side
of the sample to obtain a 1 µm-thick plate. The surface of the sample was protected from
ion damage by a Pt layer deposited on its top surface. The plate was then separated from the
rest of the electrode by cutting all three sides with the ion beam and lifted out by means of a
micromanipulator with a W-tip end attached to the plate by a thin layer of Pt. The plate lifted out in this way was attached to a Cu grid again using Pt. Finally, the thickness of the plate was further reduced to about 100 nm by polishing its surface using a low ion beam current of 10 pA to minimize the ion-beam induced damage in the TEM samples. The samples prepared using this lift-out technique was examined by TEM. These included STEM and HR-TEM studies that were performed using an FEI Titan 80-300 TEM operated at 300 kV.

7.2.4. In-situ Optical and Raman Spectroscopy during Cyclic Voltammetry Experiments

In situ observation of surface changes of Sn-CFP anodes during cyclic voltammetry (CV) experiments were carried out by placing them at the center of an electrochemical cell constructed from polytetrafluoroethylene (PTFE). Description of the experimental setup has been provided in [7]. A 99.99% pure lithium wire with a resistivity of 9.446 \( \mu \Omega \text{-cm} \) (at 20°C) was used for both counter and reference electrodes, and the electrolyte was 1 M LiClO\(_4\) in a 1:1 (by vol.) mixture of EC and 1,2-dimethoxy ethane. The top surface of the Sn-CFP anode was monitored using an optical microscope with a large depth of field. CV tests were performed between 3.00 and 0.02 V (vs. Li/Li\(^+\)), using a scan rate of 2.0 mVs\(^{-1}\).

Raman measurements were conducted in situ by replacing the optical microscope with a Raman 50× objective. A 50 mW Nd-YAG solid state laser diode, emitting a continuous wave laser at the 532 nm excitation line was used, and the spectra was recorded using a Horiba Jobin Yvon iHR 320 spectrometer equipped with a thermoelectrically cooled (-75 °C) Synapse CCD detector. The diameter of the laser spot on the specimen surface was 1 \( \mu \text{m} \).
7.3. Results

7.3.1. Capacity of Coated and Uncoated CFP

Galvanostatic charge-discharge cycling tests showed that the Sn-CFP electrode suffered an initial drop in capacity by 10% from 6.55 to 5.88 mAh cm$^{-2}$, whereas the capacity drop recorded in the first cycle was 14% for pure Sn electrodes, from 1.80 to 1.54 mAh cm$^{-2}$, and as high as 34% for uncoated electrodes, from 1.28 to 0.84 mAh cm$^{-2}$ (Fig. 7.3).

![Fig. 7.3. Variation of planar capacities of the Sn-CFP composite, pure Sn and the CFP electrodes with cycle number.](image)

The coated electrodes depicted a reversible planar capacity of 3.20 mAh cm$^{-2}$ with a capacity loss of 50% after 20 galvanostatic cycles, compared to 79% measured for Sn electrodes, and 86% for uncoated CFP electrodes. Although there was capacity loss during
initial and long-term cycling in both coated and uncoated CFP electrodes, the capacity of Sn-coated electrodes between the 2\textsuperscript{nd} and 13\textsuperscript{th} cycle was 6 times higher than Sn electrodes and 13 times higher than the uncoated ones. For the coated electrodes, the loss in the capacity after the 13\textsuperscript{th} cycle was attributed to the coating disintegration that is discussed in the following sections.

7.3.2. SEM Observations of Cycled Uncoated-CFP and Sn-CFP

A secondary electron SEM image of the Sn-CFP electrode microstructure in as-prepared condition is shown in Fig.7.4 (a). The carbon fibres were uniformly covered by Sn

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.4.png}
\caption{(a) SEM image of the Sn-CFP electrode in as-prepared condition. (b) EDS map of the area shown in (a) with C shown as yellow and Sn shown as purple. (c) Back-scattered SEM image of the Sn-CFP electrode microstructure after 20 cycles. (d) EDS map of the area shown in (c).}
\end{figure}
as indicated by the corresponding EDS map [Fig.7.4 (b)] of Sn and carbon. A back-scattered electron micrograph of the Sn-CFP electrode after twenty charge-discharge cycles is presented in Fig.7.4 (c) and reveals considerable change in the morphology of the electrode. The EDS map of Sn and carbon is represented in Fig.7.4 (d). This EDS map shows the Sn layer, which uniformly coated the carbon surfaces before the cycling tests, was stripped off.

![Fig.7.5](image)

*Fig.7.5. SEM images showing (a) uncoated and (b) Sn-coated fibres after cycling.*
the carbon fibres in some areas, exposing sections of carbon fibers. The Sn particles that were removed from the surfaces of the carbon fibres were mixed in the matrix consisting of the electrolyte reduction products and occupied the microscopic pores between the carbon fibres [37].

At high magnifications, the microstructures of uncoated and coated carbon fibres after electrochemical cycling were particularly revealing. The uncoated fibres after cycling showed extensive damage by means of exfoliation of the fibres’ surfaces [Fig.7.5 (a)]. On the other hand, coated CFP electrodes depicted severe fragmentation of the Sn coating after cycling. Removal of Sn by fragmentation resulted in exposure of the fibres’ surfaces [Fig.7.5 (b)], but the fibres themselves remained undamaged. These observations necessitated a closer examination of the cross-sections of the cycled Sn-coated carbon fibers by high resolution TEM to understand the degradation mechanisms.

7.3.3. TEM Characterization of Electrochemically Cycled Sn-CFP

It was seen in Section 7.3.2 that the carbon fibres were exposed since the Sn coating was comminuted into fragments during prolonged cycling and mixed with the electrolytic reduction products (Fig.7.4). The cross-section of a coated carbon fibre and the surrounding matrix after electrochemical cycling is shown in the STEM image in Fig.7.6 (a). The damage to the Sn coating was extensive, whereas the carbon fibre itself exhibited negligible damage. The coating in this particular section was almost completely detached and fragmented into Sn particles having sizes in the range of 4-100 nm. In some regions, the fragmented particles agglomerated to form 0.5-2.0 μm sized Sn clusters. The particles and clusters were dispersed in the SEI between the carbon fibres. The high-resolution TEM image of the matrix obtained from a region marked as (b) in Fig.7.6 (a) and shown in Fig.7.6 (b) displays periodic crystalline lattice structure that could be observed at certain locations. Within these crystals,
Fig. 7.6. (a) A cross-sectional STEM image showing Sn-coated carbon fibres after cycling having clustered and isolated Sn particles scattered in a porous matrix. (b) HR-TEM image of disintegrated Sn nanoparticles in the amorphous matrix. Inset shows a FFT-derived diffraction pattern indicating the co-existence of Sn and Li$_2$CO$_3$. 
the lattice spacings corresponded to the \{200\} planes of Sn, where the distance between the planes was measured as 0.29 nm. In another 4 nm sized crystal, interplanar spacing measured as 0.21 nm corresponded to the \{220\} planes of Sn. These fragmented Sn particles were dispersed in an amorphous matrix. FFT-derived diffraction pattern (inset) of another crystalline domain marked in Fig.7.6 (b) indicated the co-existence of Sn particles and Li₂CO₃ that formed during the reduction of the EC-containing electrolyte [45]. Therefore, the fragmented Sn particles were mixed with the electrolyte decomposition products. The particles and clusters, dispersed in the micro-pores between the carbon fibres, possibly provided additional mechanical stability and formed a Li-ion conductive network in the composite anode and, therefore, enhanced the capacity of Sn-coated CFP anodes.

7.4. Discussion

7.4.1. Surface Changes in Sn-CFP Observed in the Time Scale of Electrochemical Tests

Both the Sn and carbon components of the Sn-CFP anodes contribute to the performance of the Li-ion cell; Sn enhances the capacity, while carbon improves the mechanical stability of the cell. Therefore, the Sn-carbon composite anodes have an advantage over pure Sn or graphite anodes. However, the lithiation/de-lithiation cycles had adverse effects on the Sn coating. The surface changes that take place in each of these components during the electrochemical cycling are discussed in this section to provide an understanding of the degradation mechanisms of the Sn-CFP anodes. Optical microscopical observations of the initial surface of Sn-CFP electrodes as observed through the glass window in the cell can be seen in Fig.7.7 (a). Prior to testing, the diameter of the Sn-coated fibres was measured as 9.00±0.26 \(\mu\)m. CV experiments were conducted from \(V = 3.00\) V to 0.02 V (vs. Li/Li⁺) in which a high voltage of 3.00 V was applied initially during CV tests and
Fig. 7.7. Optical micrographs obtained in situ at 1000× during CV experiments with Sn-coated CFP electrodes: (a) at the beginning of the test (3.00 V), after (b) 1 cycle, (c) 10 cycles, (d) 19 cycles, (e) 28 cycles and (f) 42 cycles.
the voltage was decreased to 0.02 V at a constant scan rate of 2.0 mVs⁻¹. The surface changes that occurred during the CV tests were particularly revealing. During progressive cycling it was observed that the average diameter of the fibres increased to 11.60±0.35 μm at the end of the 1st cycle [Fig.7.7 (b)], 13.92±0.44 μm at the end of the 10th cycle [Fig.7.7 (c)], 22.55±6.08 μm at the end of the 19th cycle [Fig.7.7 (d)], 25.30±6.43 μm at the end of the 28th cycle [Fig.7.7 (e)], and 30.77±4.00 μm at the end of the 42nd cycle [Fig.7.7 (f)]. Increase in the fibre diameter was attributed to the lithiation/de-lithiation induced volume changes in the Sn coating. For single crystal anodes [47,48], it has been suggested that anisotropic volume changes in the grains of the Sn coating could lead to fragmentation of the coating into individual Sn grains. Fragmented Sn particles were also observed in cycled Sn-CFP anodes (Fig.7.6). The changes in the surface structure of Sn-CFP were further analyzed using micro-Raman spectroscopy during these tests.

Raman spectra were recorded at the end of each cycle (at 3.00 V), and the selected spectra are shown in Fig.7.8. The spectra obtained during cycling consisted of peaks between 1400 and 1500 cm⁻¹, due to the vibrations of various C-H bonding modes of EC [38]. With progressive cycling, the intensity of the Raman G-band peak at ~1581 cm⁻¹, arising due to bond stretching of the carbon \( sp^2 \) atoms in the CFP substrate [39,40], increased. The depth of penetration of the 532 nm laser beam is less than 100 nm [41]. Hence, the increase in the 1581 cm⁻¹ peak intensity indicated gradual decrease in the thickness of the Sn coating (500±100 nm) due to its disintegration and exposure of CFP substrate. Apart from the 1581 cm⁻¹ peak, another peak at 1350 cm⁻¹ appeared after the 40th cycle. The 1350 cm⁻¹ peak (D-band) is associated with the structural characteristics of the exposed CFP surfaces and corresponds to a reduction in the crystallinity and imperfections in the graphitic structure [40,42,43]. Therefore, the increase in the 1350 cm⁻¹ peak intensity was attributed to the
damage in the CFP surfaces possibly due to an increased rate of Li-ion diffusion into the exposed fibres. The changes in the carbon fibre lattice spacings due to increased Li-ion diffusion distances have been discussed in Section 7.4.2.

Fig. 7.8. A series of Raman spectra obtained in situ during CV experiments with Sn-coated CFP electrodes. Increase in the G-band (1581 cm\(^{-1}\)) peak intensity after 19 cycles indicated disintegration of the Sn coating and exposure of the CFP substrate.
7.4.2. Li-Ion Diffusion in Coated and Uncoated Fibres

HR-TEM images obtained from surface and near-surface regions of coated and uncoated fibres revealed slight variations in the spacing between the graphite planes. The $d$-spacings of the graphite (002) planes measured before and after the electrochemical cycling were not identical. The measurements were performed from diffraction patterns obtained along the fibre’s radius, i.e., immediately underneath the surface, a location about 0.75 µm under the surface, and the central area (about 3.75 µm away from the surface). The measured (002) $d$-spacing values are plotted in Fig.7.8.

![Graph showing $d$-spacing values](image)

**Fig.7.9.** The $d$-spacing values of the graphite (002) planes in the carbon fibres for the CFP and the Sn-coated CFP anodes measured along the radius of the fibres before and after the electrochemical cycling.
The $d$-spacing values were all larger than the commonly quoted value of 0.335 nm [46], but they slightly decreased when moving toward the centre of the fibres. At the surface, a $d$-spacing of 0.350±0.004 was measured for the fibres prior to the electrochemical test. Galvanostatic cycling caused an increase in the $d$-spacing to 0.356±0.002 nm for uncoated fibres, and 0.358±0.004 nm for Sn-coated ones. The increase in the $d$-spacing was attributed to the diffusion of Li-ions between the planes adjacent to the fibres’ surfaces. In the case of the uncoated fibres, the difference in the pre- and post-cycling $d$-spacing remained constant at 0.006-0.007 nm along the fibres radii. In the case of the Sn-coated fibres, however, the $d$-spacing difference was much smaller at the centre (i.e., 0.001 nm) compared to that at the surface (i.e., 0.008 nm). Thus, the Sn coating reduced the Li-ion diffusion distance into the carbon substrate.

7.4.3. Mechanisms of Capacity Retention in Coated and Uncoated Fibres

Schematic drawings providing an interpretation of the damage mechanisms of Sn-coated, bulk Sn and uncoated CFP anodes due to electrochemical cycling in Li-ion cells are presented in Fig.7.10. The capacity changes of Sn-CFP electrodes can be classified into three stages. In Stage 1 (first cycle), it was observed that the capacity of Sn-CFP was higher compared to that of bulk Sn and uncoated CFP electrodes. The increased first cycle capacity of Sn-CFP was attributed to the magnitude of the exposed surface area of the coated fibres, $6.87 \times 10^7 \ \mu m^2$, which was approximately 2.2 times higher than that of bulk Sn ($3.14 \times 10^7 \ \mu m^2$). The increased surface area due to the nanostructured morphology of the Sn-coated electrodes led to an increase in the energy density and, hence, an increase in the electrochemical capacity. Therefore, it is expected that the first cycle capacity of a composite anode consisting of fibres would depend on their density ($\rho_{fibre}$), that is the number of fibres present per unit volume, and can be described as,
\[ C_{\text{composite}} = C_{\text{Sn}} + \left(7.9 \times 10^5\right)\rho_{\text{fiber}}C_{\text{Sn}} \]  \hspace{1cm} (7.1)

where, \( C_{\text{composite}} \) is the electrochemical capacity of the composite anode, and \( C_{\text{Sn}} \) is the capacity of pure or bulk Sn electrodes.

After Stage 1, the capacity-declining rate was very low \((1.7 \times 10^{-2} \text{ mAh cm}^{-2} \text{ cycle}^{-1})\) in Stage 2. In this stage, the Sn-coating was able to protect the carbon fibres from exfoliation as seen in Fig. 7.5 (b). In fact, the Sn coating could reduce the rate of Li-ion diffusion into the carbon fibres that led to a smaller increase in the \( d \)-spacing of the (002) planes along the radius of the fibres (Fig. 7.8). Negligible damage occurring in the fibres suggested that the fibre network in the Sn-CFP anode continued to act as both current collector and active material. In Stage 3, the Sn coating fragmented into nano-sized particles and mixed with the electrolyte reduction products [Figs. 7.4 (c) and (d)]. Fragmentation, which was attributed to volume changes induced by lithiation/de-lithiation, could also cause isolation of regions in Sn that formerly contributed to the lithiation/de-lithiation processes and, therefore, lead to the capacity drop (Fig. 7.3). Occasionally, the fragmented particles coagulated to form clusters. It was also observed that coating disintegration caused exposure of the fibres, which resulted in damage of the graphitic structure (Fig. 7.8). Although damage of the Sn coating and the fibres caused a significant reduction in the capacity of the cell after 13 cycles (Fig. 7.3), dispersion of these particles within the pores between the carbon fibres could provide additional conduction paths for Li-ions in addition to providing mechanical stability. Therefore, the capacity of Sn-CFP anodes observed in Stage 3 was still higher than that observed in case of bulk Sn electrodes. On the other hand, Stages 2 and 3 were inconspicuous for bulk Sn and uncoated carbon fibres. Electrochemical cycling would cause extensive damage by mud-crack formation [37] in bulk Sn electrodes, or exfoliation of the
Fig. 7.10. Schematic diagram showing the capacity fading mechanisms of Sn-coated, bulk Sn and uncoated CFP anodes. The increased capacity of Sn-CFP in Stage 1 was due to their large surface area compared to bulk Sn electrodes. The low rate of capacity fading of Sn-CFP in Stage 2 was attributed to protection of the fibres by the Sn-coating. In Stage 3, the capacity declined rapidly since electrochemical cycling caused disintegration of the coating. In comparison, ‘mud crack’ formation in bulk Sn and exfoliation of uncoated fibres would lead to a high capacity fading rate immediately after Stage 1.
surfaces of carbon fibres [Fig.7.5 (a)] resulting in a high capacity-declining rate immediately after Stage 1.

The observations in the present study suggest that the microstructure and morphology of Sn and carbon components in Sn-carbon composite anodes may greatly influence the microscopical changes that take place in both Sn and carbon during electrochemical cycling and hence, may play a significant role in the performance of these anodes in Li-ion cells. For instance, a small initial grain size of Sn coating may be beneficial in two ways: i) during the initial cycles, the cracking and delamination of the coating from the current collector is delayed compared to a coating with a larger grain size [11,26]; and ii) the fragmentation of the coating into smaller particles during the initial cycles may create a conductive network of nanoparticles in the matrix that forms around the carbon component of the anode, resulting in an anode with a better Li-ion conductivity.

7.5. Conclusions

The electrochemical degradation mechanisms of a Sn-carbon fibre composite (Sn-CFP) anode, which was fabricated by electrodepositing an ultrafine-grain (~350 nm) Sn coating on a carbon fibre paper (CFP), were studied by cycling in a Li-ion cell. The main findings of this study are as follows:

1. The capacity changes of Sn-CFP electrodes were classified into three stages. The capacity of Sn-CFP, 6.55 mAhcm$^{-2}$, was higher compared to that of bulk Sn, 1.80 mAhcm$^{-2}$, and uncoated CFP electrodes, 1.28 mAhcm$^{-2}$, in Stage 1 (first cycle). The increased first cycle capacity of Sn-CFP was attributed to the magnitude of the exposed surface area of the coated fibres, $6.87 \times 10^7 \, \mu\text{m}^2$, which was approximately 2.2 times higher than that of bulk Sn ($3.14 \times 10^7 \, \mu\text{m}^2$). The increased surface area of the
nanostructured Sn-coated surfaces led to an increase in the energy density and, therefore, an increase in the electrochemical capacity.

2. The capacity-declining rate of Sn-CFP anodes was very low in Stage 2. The Sn coating protected the graphitic structure by reducing the rate of Li-ion diffusion into the CFP substrate that led to a smaller increase in the d-spacing of the (002) planes along the radius of the fibres. Negligible damage observed in the fibres suggested that the fibre network continued to act as both current collector and active material.

3. In Stage 3, the Sn coating fragmented into 4-100 nm sized particles that were dispersed within the pores between the carbon fibres. Occasionally, the fragmented particles coagulated to form 0.5-2.0 \( \mu \text{m} \) sized clusters in the amorphous matrix of the solid electrolyte interface (SEI). The coating disintegration caused exposure of the fibres, which resulted in damage of the graphitic structure. In spite of damage of the Sn coating and the fibres, the capacity of Sn-CFP anodes observed in Stage 3 was higher than that observed in case of bulk Sn electrodes. The increased capacity was attributed to the formation of additional Li-ion conduction paths by the dispersed Sn nano-particles in the SEI.

4. For bulk Sn and uncoated carbon fibres, Stages 2 and 3 were inconspicuous. Electrochemical cycling induced damage in bulk Sn and uncoated carbon fibre electrodes resulted in a high capacity-declining rate at the end of Stage 1.

**Bibliography**


[34] C. Arbizzani, S. Beninati, M. Lazzari, M. Mastragostino, Carbon paper as three-dimensional conducting substrate for tin anodes in lithium-ion batteries, J. Power Sources, 141 (2005) 149-55.


CHAPTER 8: Summary and Conclusions

8.1. Summary of Main Results

Li-ion batteries are being increasingly considered for hybrid and pure electric vehicles apart from their use in portable electronic devices. Development of Li-ion batteries will help increase the driving range of electric vehicles more than that of conventional gasoline vehicles. Damage of the commercially used graphite anodes in these batteries is a performance-limiting factor and would lead to capacity fading. Microstructural investigations of the degradation mechanisms in graphite during charging and discharging of Li-ion batteries will help to design the ideal anode with high durability and capacity. This research was aimed at developing new testing instruments and a novel experimental methodology for identifying the mechanisms of surface and subsurface damage in graphite electrodes. The microstructural information was correlated to the electrochemical performance in order to develop new design methods for producing improved electrodes.

8.1.1. Instantaneous Damage in Graphite Electrodes

Damage that occurs on graphite electrode surfaces in the first cycle during electrochemical cycling, simulating lithium-ion battery conditions, was observed in-situ using a digital microscope. Microscopical evidence revealed extensive particle removal during delithiation stage and continued until the potential difference, exerted on graphite, reduced beyond a critical value. The rate of graphite particle loss increased at a lower voltage scan rate. Experiments, initiating from the peak voltage, promoted formation of a surface film (SEI) on graphite that reduced graphite degradation during the course of lithiation.
8.1.2. Damage Accumulation during Progressive Cycling

Subsurface defects and local compositional changes that occurred in graphite anodes during progressive cycling were investigated using HR-TEM techniques. Cross-sections of anodes prepared by FIB milling indicated that graphite layers adjacent to SEI/graphite interface exhibited partial delamination due to formation of interlayer cracks. The SEI layer formed on the graphite surface consisted of Li$_2$CO$_3$ that was identified by means of {110} and {002} crystallographic planes. Lithium compounds, LiC$_{6}$, Li$_2$CO$_3$ and Li$_2$O, were observed on the surfaces of separated graphite layers. Deposition of these co-intercalation compounds near the crack tip caused partial closure of propagating graphite cracks during electrochemical cycling, and possibly reduced the crack growth rate. Graphite layers that were observed to bridge crack faces provided an additional mechanism for the retardation of crack propagation.

8.1.3. Micromechanisms of SEI Formation

The microstructural and compositional changes that occurred in the SEI formed on graphite electrodes subjected to voltammetry tests at different voltage scan rates were investigated. The microstructure of SEI layer, characterized using HR-TEM, consisted of an amorphous structure incorporating crystalline domains of ~ 5-20 nm in size. Evidence of lithium compounds, namely Li$_2$CO$_3$ and Li$_2$O$_2$, and nano-sized graphite fragments were found within these crystalline domains. The morphology and thickness of the SEI depended on the applied $dV/dt$. The variations in the $D_{Li}^+$ at the electrode/electrolyte interface during the SEI formation process were measured and two regimes were identified depending on the scan rate; for $dV/dt \geq 3.00$ mVs$^{-1}$, $D_{Li}^+$ was $3.13 \times 10^{-8}$ cm$^2$s$^{-1}$. At lower scan rates where $D_{Li}^+$ was low ($0.57 \times 10^{-8}$ cm$^2$s$^{-1}$), a uniform and continuous SEI layer was formed.
8.1.4. Capacity Enhancement by Pre-treatment at 60°C

Graphite electrodes were electrochemically cycled in Li-ion cells at 50 and 60°C in order to determine the changes in their surface properties in comparison to the electrodes tested at 25°C. A 17% drop in planar capacity occurred during the first cycle at 60°C compared to a 40% at 25°C and reduced the amount of damage occurred to graphite due to a rapidly formed SEI. During the following cycles, a planar capacity of 3.11±0.12 mAhcm\(^{-2}\) was attained at 60°C rather than 0.53±0.03 mAhcm\(^{-2}\) at 25°C. The SEI layer formed at 60°C predominantly consisted of Li\(_2\)CO\(_3\) and was devoid of residual LiClO\(_4\) detected at 25°C. At 25°C, \(D_{Li^+}\) was calculated as 1.07×10\(^{-8}\) cm\(^2\)s\(^{-1}\), whereas at 60°C, \(D_{Li^+}\) increased to 3.25×10\(^{-8}\) cm\(^2\)s\(^{-1}\). A pre-treatment conducted at 60°C enhanced the cyclic performance of graphite subsequently cycled at 25°C; a Li\(_2\)CO\(_3\)-enriched SEI, generated during the 60°C pre-treatment, covered the graphite surface uniformly and ensued a 28% increase in battery capacity at 25°C.

8.1.5. Improvement of Electrochemical Cycling Behaviour of Graphite Anodes by Li\(_2\)CO\(_3\) Pre-treatment

In Chapter 5, it was observed that the presence of Li\(_2\)CO\(_3\) in the SEI is beneficial as it improves the capacity at 25°C. Therefore, prior to cycling, graphite electrodes were treated using a simple process of sedimentation in aqueous solutions containing 0.5 and 1.0 wt.% Li\(_2\)CO\(_3\) with particle sizes of \(~1-2\mu m\). During the first cycle of voltammetry tests (vs. Li/Li\(^+\)), the graphite surface was subjected to electrochemical degradation as a result of fracture and removal of near-surface graphite particles. Surface degradation was accompanied by a 0.4% strain in the graphite lattice as determined by \textit{in situ} Raman spectroscopy. Pre-treated electrodes experienced a capacity drop of 3% in the first cycle, compared to a 40% drop observed in case of untreated graphite electrodes. After testing for
100 cycles, a high capacity of 0.54 mAh cm\(^{-2}\) was recorded for pre-treated electrodes as opposed to a significant drop to 0.11 mAh cm\(^{-2}\) for the untreated graphite. Cross-sectional HR-TEM indicated that the SEI formed on pre-treated electrodes primarily consisted of Li\(_2\)CO\(_3\) crystals of 14.6±6.9 nm in size distributed within an amorphous matrix. The results suggested that the Li\(_2\)CO\(_3\) enriched SEI formed on pre-treated electrodes reduced the intensity of solvent co-intercalation induced surface damage. It was proposed that the Li\(_2\)CO\(_3\) enriched SEI facilitated Li\(^+\) diffusion and hence improved the capacity retention during long-term cycling.

8.1.6. Sn-Carbon Fibre Composite Anodes for Li-ion Batteries

Sn-carbon fibre composite anodes (Sn-CFP) were fabricated by electrodepositing an ultrafine-grain (~350 nm) Sn coating on a carbon fibre paper, and electrochemically cycled in a Li-ion cell to study the capacity degradation mechanisms. Electrochemical capacity changes of the Sn-CFP anodes occurred in three stages. In Stage 1 (first cycle), the increased first cycle capacity of Sn-CFP (6.55 mAh cm\(^{-2}\)) was attributed to the 2.2 times higher surface area than that of bulk Sn which depicted a capacity of 1.80 mAh cm\(^{-2}\). A low capacity-declining rate of Sn-CFP anodes in Stage 2 was attributed to the protection of the CFP by the Sn-coating that reduced the rate of Li-ion diffusion and prevented expansion of the carbon (002) planes. Ultimately, the Sn coating fragmented into 4-100 nm sized particles (Stage 3) and dispersed within the pores between the carbon fibres. The coating disintegration caused exposure of the fibres, which resulted in damage of the graphitic structure. However, the capacity of Sn-CFP anodes was higher than that observed in case of bulk Sn electrodes in Stage 3. The increased capacity was attributed to the formation of additional Li-ion conduction paths by the dispersed Sn nano-particles in the SEI. For bulk Sn and uncoated
carbon fibre anodes, cycling induced damage resulted in a high capacity-declining rate after Stage 1.

8.2. General Conclusions

8.2.1. Electrode Damage Map (EDM) and its Applications

Electrochemical cycling experiments performed in this dissertation helped to determine the fraction of the cavities and fragmented particles on electrode surfaces together with the morphological changes that occurred during the SEI formation. In order to provide a quantitative summary of the results using temperature and the scan rate as the axes for a given electrolyte composition and cycle time, an electrode damage map (EDM) was constructed as seen in Fig.8.1.

![Electrode damage map of polycrystalline graphite electrodes cycled in EC-containing electrolyte.](image)

Fig.8.1. Electrode damage map of polycrystalline graphite electrodes cycled in EC-containing electrolyte.
The EDM indicates the damage regime at high scan rates and ambient temperature conditions. However, the SEI formed at higher temperature is stable, uniform and protects the graphite surface from damage. The EDM will thus provide an effective way of summarizing the relationships between the parameters that cause electrode damage, in addition to providing useful guidelines for designing improved electrode materials by defining the 'safe' operating conditions for a given electrode system.

8.2.1. Scientific and Technological Impact

This research showed that the battery electrode damage by removal of the surface graphite fragments is the most intense during the first cycle that led to a drastic capacity drop. The intensity of damage increased with the voltage scan rate. Once the SEI layer covered the electrode surface, the rate of graphite particle loss decreased. Also, the morphology and the composition of the SEI had an impact on the capacity at different temperatures. The following points should be considered for enhancing the capacity of next-generation Li-ion batteries:

1. During the first charging, low voltage scan rates (<0.05 mVs⁻¹) should be used for producing a uniform SEI that could reduce electrode damage.

2. Pre-cycling electrodes at 60°C would cause formation of a Li₂CO₃-enriched SEI and increase the battery capacity at 25°C.

3. The SEI formed on electrodes pre-treated with Li₂CO₃ particles would reduce the first cycle damage as well as promote Li-ion diffusion and improve the capacity retention of Li-ion batteries during long-term cycling.
8.3. Future Work

8.3.1. Fracture Mechanics Analyses of Crack Growth

Crack formation mechanisms in graphite anodes include separation of graphite planes due to the intercalation products diffusing at the edges of the exfoliated planes [1]. According to recent observations in Chapter 3, the solvents’ adsorption stage was instantaneous so the crack initiation occurred immediately after the application of a voltage gradient. However, the crack growth process was gradual and displayed cyclic growth properties. In fact, crack growth appeared to be controlled by the adjacent partially delaminated graphene planes bridging the faces of the main crack and the intercalation products at the tip preventing the crack from fully closing (Figs. 3.9 and 3.10). Thus, a fracture mechanics approach will be a valuable tool to rationalize the crack growth process. For example, the value of cyclic stress intensity factor $\Delta K (= K_{\text{max}} - K_{\text{min}})$ that controls the growth rate $(da/dN)$ of an initial crack of length $(a)$ during each cycle $(N)$ of a CV test will be reduced to a lower value of $\Delta K_{\text{effective}}$ due to partial closure of the crack tip in the presence of intercalation products at crack faces (i.e., $K_{\text{closure}} > K_{\text{min}}$). Consequently in the presence of intercalation deposits as $\Delta K_{\text{effective}} < \Delta K$, then a low $da/dN$ can be attained after the first cycle.

A single edge notched beam (SENB) sample with an FIB-milled atomically sharp crack at the EDM cut notch tip would constitute a useful configuration for $\Delta K$ measurements for which $(da/dN)$ can be determined during the CV tests using an optical microscope. Samples with pre-existing SEI layers can be studied in this way to elucidate the protective nature of the SEI on crack propagation. For example, a threshold value of $K_{\text{th}}$ below which no crack growth can occur will be determined and the sensitivity of $K_{\text{th}}$ to the
solvent composition and temperature will be clarified. In addition, important details such as the transport mechanisms of electrolytes with different viscosities, and diffusion mechanisms that influence C-C bond breaking during crack growth can be clarified with the aid of the TEM. Thus, these fracture mechanics experiments are expected to contribute to an understanding of the atomic- and micro-mechanisms of electrode damage processes.

8.3.2. Electrochemical Properties of Mesocarbon Microbeads (MCMB)

Carbonaceous materials can be classified as unorganized, turbostratic or graphitized solid, according to their structures. The lithium intercalation capacity of each of these forms is different. The less organized forms can be classified into soft (graphitizes at $t \leq 2000^\circ C$) or hard carbons (graphitizes at $t > 2800^\circ C$). Soft carbons like mesocarbon microbeads (MCMB) have good capacity at low voltage and good cyclability [2,3]. It consists of roughly spherical structures with an average diameter of 15.5 $\mu$m diameter and consequently, 99.5% lower specific surface area. The observed capacity could reach values as high as 750 mAh/g [4] that is $2 \times$ greater than graphite (372 mAh/g for LiC$_6$). Thus maximizing the surface area and altering surface topography are expected to accelerate intercalation kinetics and hence investigations will also embrace MCMB electrodes.

MCMB electrodes were prepared by ultrasonic mixing of 90 wt.% graphite powder and 10 wt.% PVDF (binder) in 1-Methyl-2-pyrrolidinone. The slurry was applied on a Cu base and dried overnight at 105°C. The electrodes were stored in Argon before installation in the cell. The microstructure of the prepared MCMB particles can be seen in Fig.8.2 (a). Electrochemical cycling of MCMB was performed using EC- and PC-based electrolytes and in both cases, the SEI formed on the MCMB particles revealed a spherical morphology (Figs.8.2 (b) and (c)).
Cross-sectional microstructure obtained by FIB milling showed that the subsurface damage in MCMB particles was negligible when cycled in EC (Fig. 8.3 (a)). However, electrochemical cycling in PC-electrolytes caused partial delamination of the graphite layers as can be seen in (Fig. 8.3 (b)).

In addition, a bright-field TEM image in Fig. 8.3 (c) revealed that the thickness of the SEI formed on the MCMB particles was very low, i.e., 450.0±141.4 nm, compared to the SEI formed on polycrystalline graphite electrodes (1.02±0.15 μm) as seen in Section 4.3.3. Further CV experiments performed using MCMB electrodes at low to high $dV/dt$ and temperatures will help to correlate the $D_{Li^{+}}$ operating at the particle/electrolyte interface to the microstructure, morphology and composition of the SEI layers that, in turn, controls the electrochemical performance of battery electrodes.
8.3.3. Damage Mechanisms of Si particles in Al-Si Electrodes

There is great interest in developing rechargeable lithium-ion batteries with higher energy capacity and longer cycle life for applications in electric vehicles and implantable medical devices [5]. Silicon is an attractive anode material for lithium-ion batteries because it has a low discharge potential and the highest known theoretical charge capacity (4,200 mAh/g for Li$_{21}$Si$_5$ [6]). Although this is more than ten times higher than the existing graphite anodes, silicon anodes have limited applications [7] because silicon’s volume changes by 400% upon insertion and extraction of lithium which results in pulverization and capacity fading [2]. It is expected that the ductile Al-matrix in an Al-Si alloy could mitigate the volume expansion and prevent accumulation of strain in Si particles that causes fracture.
Microstructural observations of the electrode surface obtained in-situ were particularly interesting. Fig.8.4 (a) shows a selected region on the electrode before initiating the test. More specifically, the changes in the polygonal-shaped Si particle located at the center of the microstructure were monitored during cycling. At the end of the first cycle [Fig.8.4 (b)], globular deposits were observed to form at the Si-Al interfaces. These deposits could be products of the electrolyte reduction process during the SEI formation. The size and number of the globules grew with progressive cycling as observed at the completion of the fifth cycle in Fig.8.4 (c). The amount and size of these products was observed to be more when cycled in presence of EC. In case of cycling in PC-based electrolyte, the microstructure of the electrode surface prior to cycling can be seen in Fig.8.4 (d). Apart from the formation of the globular deposits (Fig.8.4 (e)), a fine network of cracks was formed on the Si particle within five cycles (Fig.8.4 (f)). These cracks originated from the Si-Al interface and propagated towards the interior of the particles. However, such cracks were absent in the particle cycled in an EC electrolyte [Fig.7.4 (c)]. It is suggested that the aggressive nature of PC [3-6], due to PC co-intercalation in Si, caused crack formation in Si even within five cycles. More study is required to understand the difference in the mechanisms of EC/PC and Li-ion intercalation in Si during electrochemical cycling.
Fig. 8.4. Optical microstructures obtained in-situ at 1000× in EC-electrolyte (a) before the test, after (b) the first and (c) the fifth cycles, and in PC-electrolyte (d) before the test, and after (e) the first, and (f) the fifth cycles.

Apart from optical microscopical observations, the effect of electrochemical cycling on the surface changes of the particles was also measured using optical interferometry. A 3-dimensional optical profilometry image of the Si particle, shown in Fig.8.4 (a), has been presented in Fig.8.5 (a). After cycling in EC-containing electrolyte, surface SEI deposits were
observed to form on the particles’ surfaces that were noted as small chunks in the
profilometry image in Fig.8.5 (b).

![3D optical profilometry images](image)

**Fig.8.5.** 3-dimensional optical profilometry images of a Si particle obtained at 20× (a) before cycling and (b) after cycling in EC-electrolyte for five cycles. (c) Comparison of 2-dimensional profiles of the same particle obtained before and after cycling.

Before cycling, the Si particle surface was relatively smooth with the surface roughness, measured over an area of approximately 42 μm², varying between 63-65.0 nm. The height of the profile obtained after cycling was comparable to the one before, but showed the presence of 2.0-2.5 μm high spikes that were due to the SEI deposits. In addition, the
surface roughness of the particles increased to 139.3 nm that was measured over the same area.

![Fig.8.6. 3-dimensional optical profilometry images of a Si particle obtained at 20× (a) before cycling and (b) after cycling in PC-electrolyte for five cycles. (c) Comparison of 2-dimensional profiles of the same particle obtained before and after cycling.](image)

In case of cycling in PC-electrolytes, the 3-dimensional profilometry image of a Si particle before cycling is shown in Fig.8.6 (a) and after five cycles is shown in Fig.8.6 (b). Further analyses of the morphological changes in the selected particles were performed using 2-dimensional profiles in Fig.8.6 (c) that were obtained along the line indicated as A-B in Figs.8.6 (a) and (b). In this case, the surface roughness of Si changed from 65.0 nm to 167.1 nm after cycling. The higher increase in surface roughness after cycling in presence of PC
was due to more damage induced by co-intercalation of PC molecules. In case of cycling in a PC-containing electrolyte, the number and height of the SEI deposits was less as can be seen in Fig.8.6 (c). The height of the deposits varied between 0.8-1.0 μm. However, the particle height after cycling decreased by 0.25 μm. The differences in the heights of the same particle before and after cycling were attributed to loss of Si due to aggressive nature of the electrolyte.

Apart from the surface changes, lithiation of Si also resulted in a change in its crystal structure which was measured using Raman spectroscopy. During lithiation of Si, each Si atom may be surrounded by several Li atoms. It has been reported that the insertion of lithium-ions into Si could destroy the bonds among Si atoms [8,9]. The changes in the crystal structure of the Si particles during electrochemical lithiation/de-lithiation cycles were studied by performing in-situ Raman spectroscopy. Fig.8.7 (a) shows a series of Raman spectra of Si that were obtained in the first cycle in EC-electrolyte. A sharp and prominent peak at 518 cm$^{-1}$ occurring due to the lattice vibration mode of diamond-cubic Si (Si-I) was observed in the beginning at 3.00 V. As the voltage was decreased, the intensity of the Si-I peak diminished and completely disappeared at the lowest voltage value, 0.02 V. Thus, insertion of lithium ions into Si resulted in the formation of an amorphous structure.

Interestingly when the voltage increased again to 3.00 V, the Raman peak due to Si-I reappeared. Thus the phase transformation of Si from crystalline diamond cubic to the amorphous structure was reversible in nature. However it can be observed in Fig.7.7 (b) that the intensity of the Si-I peak at the beginning of the second cycle (3.00 V) was less than that observed at the beginning of the first cycle. The decrease in the Si-I peak intensity was
Fig. 8.7. In-situ micro-Raman spectra obtained from Si during the first and second cycles in EC-electrolyte.

attributed to the partially disordered Si lattice due to lithium insertion/extraction. As the voltage was changed from 3.00 → 0.02 → 3.00 V, Si transformed from crystalline → amorphous → crystalline. Further crystallographical analyses using TEM samples excised
from cycled electrodes will help to compare the $d$-spacing changes in Si at 3.00 V and 0.02 V. Electrochemical capacity calculations using the Si-Al electrodes will elucidate the feasibility of their usage as anodes in lithium-ion batteries.

**Bibliography**


APPENDIX: Copyright Releases from Publications

CHAPTER 2

In-situ Observations of Lithiation/de-lithiation Induced Graphite Damage During Electrochemical Cycling

ELSEVIER LICENSE: TERMS AND CONDITIONS

November 18, 2013

This is a License Agreement between Sandeep Bhattacharya ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier: Elsevier Limited, The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK

Registered Company Number: 1982084

Customer name: Sandeep Bhattacharya

Customer address: University of Windsor, 401 Sunset Avenue, Windsor, ON N9B3P4

License number: 3271751156638

License date: November 18, 2013

Licensed content publisher: Elsevier

Licensed content publication: Scripta Materialia

Licensed content title: In-situ observations of lithiation/de-lithiation induced graphite damage during electrochemical cycling
INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions
established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

**GENERAL TERMS**

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

   “Reprinted from Publication title, Vol / edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER].” Also Lancet special credit - “Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier.”

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's
Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

**LIMITED LICENSE**

The following terms and conditions apply only to specific license types:

15. Translation: This permission is granted for non-exclusive world English rights only unless your license was granted for translation rights. If you licensed translation rights you
may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. Website: The following terms and conditions apply to electronic reserve and author websites:

Electronic reserve: If licensed material is to be posted to website, the website is to be password-protected and made available only to bona fide students registered on a relevant course if:

This license was made in connection with a course,

This permission is granted for 1 year only. You may obtain a license for future website posting,

All content posted to the web site must maintain the copyright information line on the bottom of each image,

A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com, and

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

17. Author website for journals with the following additional clauses:

All content posted to the web site must maintain the copyright information line on the bottom of each image, and the permission granted is limited to the personal version of your paper. You are not allowed to download and post the published electronic version of your article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx. As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier’s online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article’s Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
18. Author website for books with the following additional clauses:

Authors are permitted to place a brief summary of their work online only.

A hyper-text must be included to the Elsevier homepage at http://www.elsevier.com. All content posted to the web site must maintain the copyright information line on the bottom of each image. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

19. Website (regular and for author): A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or for books to the Elsevier homepage at http://www.elsevier.com

20. Thesis/Dissertation: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

21. Other Conditions:

v1.6

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501161268.

Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

Make Payment To:

Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006
For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing $0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.
CHAPTER 3

A Transmission Electron Microscopy Study of Crack Formation and Propagation in Electrochemically Cycled Graphite Electrode in Lithium-ion Cells

ELSEVIER LICENSE: TERMS AND CONDITIONS

November 18, 2013

This is a License Agreement between Sandeep Bhattacharya ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier: Elsevier Limited, The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK

Registered Company Number: 1982084

Customer name: Sandeep Bhattacharya

Customer address: University of Windsor, 401 Sunset Avenue, Windsor, ON N9B3P4

License number: 3271751079212

License date: November 18, 2013

Licensed content publisher: Elsevier

Licensed content publication: Journal of Power Sources

Licensed content title: A transmission electron microscopy study of crack formation and propagation in electrochemically cycled graphite electrode in lithium-ion cells

Licensed content author: Sandeep Bhattacharya, A. Reza Riahi, Ahmet T. Alpas

Licensed content date: 15 October 2011
INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).
GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

“Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER].” Also Lancet special credit - “Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier.”

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC’s Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC’s Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC’s Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the
materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

**LIMITED LICENSE**

The following terms and conditions apply only to specific license types:

15. Translation: This permission is granted for non-exclusive world English rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the
integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. Website: The following terms and conditions apply to electronic reserve and author websites:

Electronic reserve: If licensed material is to be posted to website, the website is to be password-protected and made available only to bona fide students registered on a relevant course if:

This license was made in connection with a course,

This permission is granted for 1 year only. You may obtain a license for future website posting,

All content posted to the web site must maintain the copyright information line on the bottom of each image,

A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com, and

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

17. Author website for journals with the following additional clauses:

All content posted to the web site must maintain the copyright information line on the bottom of each image, and the permission granted is limited to the personal version of your paper. You are not allowed to download and post the published electronic version of your article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx. As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier’s online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article’s Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

18. Author website for books with the following additional clauses:

Authors are permitted to place a brief summary of their work online only.
A hyper-text must be included to the Elsevier homepage at http://www.elsevier.com. All content posted to the website must maintain the copyright information line on the bottom of each image. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

19. Website (regular and for author): A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxxx. or for books to the Elsevier homepage at http://www.elsevier.com

20. Thesis/Dissertation: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

21. Other Conditions:

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501161266.

Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

Make Payment To:

Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006
For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing $0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.
CHAPTER 4

Micromechanisms of Solid Electrolyte Interphase Formation on Electrochemically Cycled Graphite Electrodes in Lithium-ion Cells

ELSEVIER LICENSE: TERMS AND CONDITIONS

November 18, 2013

This is a License Agreement between Sandeep Bhattacharya ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier: Elsevier Limited, The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK

Registered Company Number: 1982084

Customer name: Sandeep Bhattacharya

Customer address: University of Windsor, 401 Sunset Avenue, Windsor, ON N9B3P4

License number: 3271750889728

License date: November 18, 2013

Licensed content publisher: Elsevier

Licensed content publication: Carbon

Licensed content title: Micromechanisms of solid electrolyte interphase formation on electrochemically cycled graphite electrodes in lithium-ion cells

Licensed content author: Sandeep Bhattacharya, Ahmet T. Alpas

Licensed content date: December 2012

Licensed content volume number: 50
INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

“Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER].” Also Lancet special credit - “Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier.”

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC’s Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. Translation: This permission is granted for non-exclusive world English rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.
16. Website: The following terms and conditions apply to electronic reserve and author websites:

Electronic reserve: If licensed material is to be posted to website, the website is to be password-protected and made available only to bona fide students registered on a relevant course if:

This license was made in connection with a course,

This permission is granted for 1 year only. You may obtain a license for future website posting,

All content posted to the website must maintain the copyright information line on the bottom of each image,

A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com, and

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

17. Author website for journals with the following additional clauses:

All content posted to the website must maintain the copyright information line on the bottom of each image, and the permission granted is limited to the personal version of your paper. You are not allowed to download and post the published electronic version of your article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx. As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier’s online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article’s Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

18. Author website for books with the following additional clauses:

Authors are permitted to place a brief summary of their work online only.

A hyper-text must be included to the Elsevier homepage at http://www.elsevier.com. All content posted to the website must maintain the copyright information line on the bottom
of each image. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

19. Website (regular and for author): A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx. or for books to the Elsevier homepage at http://www.elsevier.com

20. Thesis/Dissertation: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

21. Other Conditions:

v1.6

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLINK501161262.

Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

Make Payment To:

Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006

For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.
Gratis licenses (referencing $0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.
CHAPTER 5

Thermal Cycling Induced Capacity Enhancement of Graphite Anodes in Lithium-ion Cells

ELSEVIER LICENSE: TERMS AND CONDITIONS

January 13, 2014

This is a License Agreement between Sandeep Bhattacharya ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier: Elsevier Limited, The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK

Registered Company Number: 1982084

Customer name: Sandeep Bhattacharya

Customer address: University of Windsor, 401 Sunset Avenue, Windsor, ON N9B3P4

License number: 3307160780162

License date: January 13, 2014

Licensed content publisher: Elsevier

Licensed content publication: Carbon

Licensed content title: Thermal cycling induced capacity enhancement of graphite anodes in lithium-ion cells

Licensed content author: Sandeep Bhattacharya, A. Reza Riahi, Ahmet T. Alpas

Licensed content date: February 2014

Licensed content volume number: 67
LICENSED CONTENT ISSUE NUMBER: None

NUMBER OF PAGES: 15

START PAGE: 592

END PAGE: 606

TYPE OF USE: reuse in a thesis/dissertation

PORTION: full article

FORMAT: both print and electronic

ARE YOU THE AUTHOR OF THIS ELSEVIER ARTICLE? Yes

WILL YOU BE TRANSLATING? No

TITLE OF YOUR THESIS/DISSERTATION: Degradation Mechanisms of Electrochemically Cycled Graphite Anodes in Lithium-ion Cells

EXPECTED COMPLETION DATE: May 2014

ESTIMATED SIZE (NUMBER OF PAGES): 220

ELSEVIER VAT NUMBER: GB 494 6272 12

PERMISSIONS PRICE: 0.00 USD

VAT/LOCAL SALES TAX: 0.00 USD / 0.00 GBP

TOTAL: 0.00 USD

TERMS AND CONDITIONS

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

“Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER].” Also Lancet special credit - “Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier.”

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC’s Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. Translation: This permission is granted for non-exclusive world English rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.
16. Website: The following terms and conditions apply to electronic reserve and author websites:

Electronic reserve: If licensed material is to be posted to website, the web site is to be password-protected and made available only to bona fide students registered on a relevant course if:

This license was made in connection with a course,

This permission is granted for 1 year only. You may obtain a license for future website posting,

All content posted to the web site must maintain the copyright information line on the bottom of each image,

A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com, and

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

17. Author website for journals with the following additional clauses:

All content posted to the web site must maintain the copyright information line on the bottom of each image, and the permission granted is limited to the personal version of your paper. You are not allowed to download and post the published electronic version of your article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx. As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier’s online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article’s Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

18. Author website for books with the following additional clauses:

Authors are permitted to place a brief summary of their work online only.

A hyper-text must be included to the Elsevier homepage at http://www.elsevier.com. All content posted to the web site must maintain the copyright information line on the bottom
of each image. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

19. Website (regular and for author): A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx. or for books to the Elsevier homepage at http://www.elsevier.com

20. Thesis/Dissertation: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

21. Other Conditions:

v1.6

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501200361.

Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

Make Payment To:

Copyright Clearance Center

Dept 001

P.O. Box 843006

Boston, MA 02284-3006

For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.
Gratis licenses (referencing $0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.
CHAPTER 6

Electrochemical Cycling Behaviour of Li$_2$CO$_3$ Pre-treated Graphite Anodes: SEI Formation and Graphite Damage Mechanisms

ELSEVIER LICENSE: TERMS AND CONDITIONS

May 15, 2014

This is a License Agreement between Sandeep Bhattacharya ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier: Elsevier Limited, The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK

Registered Company Number: 1982084

Customer name: Sandeep Bhattacharya

Customer address: University of Windsor, 401 Sunset Avenue, Windsor, ON N9B3P4

License number: 3390320407950

License date: May 15, 2014

Licensed content publisher: Elsevier

Licensed content publication: Carbon

Licensed content title: Electrochemical Cycling Behaviour of Li$_2$CO$_3$ Pre-treated Graphite Anodes: SEI Formation and Graphite Damage Mechanisms

Licensed content author: Sandeep Bhattacharya, A. Reza Riahi, Ahmet T. Alpas

Licensed content date: 13 May 2014
INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

“Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER].” Also Lancet special credit - “Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier.”

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

**LIMITED LICENSE**

The following terms and conditions apply only to specific license types:

15. Translation: This permission is granted for non-exclusive world English rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.
16. Posting licensed content on any Website: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

For journal authors: the following clauses are applicable in addition to the above: Permission granted is limited to the author accepted manuscript version* of your paper.

*Accepted Author Manuscript (AAM) Definition: An accepted author manuscript (AAM) is the author’s version of the manuscript of an article that has been accepted for publication and which may include any author-incorporated changes suggested through the processes of submission processing, peer review, and editor-author communications. AAMs do not include other publisher value-added contributions such as copy-editing, formatting, technical enhancements and (if relevant) pagination.

You are not allowed to download and post the published journal article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx. As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier’s online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article’s Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Posting to a repository: Authors may post their AAM immediately to their employer’s institutional repository for internal use only and may make their manuscript publically available after the journal-specific embargo period has ended.
Please also refer to Elsevier’s Article Posting Policy for further information.

18. For book authors the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. Posting to a repository: Authors are permitted to post a summary of their chapter only in their institution’s repository.

20. Thesis/Dissertation: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

**Elsevier Open Access Terms and Conditions**

Elsevier publishes Open Access articles in both its Open Access journals and via its Open Access articles option in subscription journals.

Authors publishing in an Open Access journal or who choose to make their article Open Access in an Elsevier subscription journal select one of the following Creative Commons user licenses, which define how a reader may reuse their work: Creative Commons Attribution License (CC BY), Creative Commons Attribution – Non Commercial -ShareAlike (CC BY NC SA) and Creative Commons Attribution – Non Commercial – No Derivatives (CC BY NC ND)

**Terms & Conditions applicable to all Elsevier Open Access articles:**

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author’s honour or reputation.

The author(s) must be appropriately credited.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

**Additional Terms & Conditions applicable to each Creative Commons user license:**

CC BY: You may distribute and copy the article, create extracts, abstracts, and other revised versions, adaptations or derivative works of or from an article (such as a translation), to
include in a collective work (such as an anthology), to text or data mine the article, including for commercial purposes without permission from Elsevier

CC BY NC SA: For non-commercial purposes you may distribute and copy the article, create extracts, abstracts and other revised versions, adaptations or derivative works of or from an article (such as a translation), to include in a collective work (such as an anthology), to text and data mine the article and license new adaptations or creations under identical terms without permission from Elsevier

CC BY NC ND: For non-commercial purposes you may distribute and copy the article and include it in a collective work (such as an anthology), provided you do not alter or modify the article, without permission from Elsevier

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Promotional purposes (advertising or marketing)
- Commercial exploitation (e.g. a product for sale or loan)
- Systematic distribution (for a fee or free of charge)

Please refer to Elsevier's Open Access Policy for further information.

21. Other Conditions:

v1.7

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number 501303974.

Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

Make Payment To:

Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006
For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing $0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.
VITA AUCTORIS

NAME: Sandeep Bhattacharya

PLACE OF BIRTH: Calcutta, West Bengal, India

YEAR OF BIRTH: 1982

EDUCATION:
Jadavpur University, B.E., Calcutta, West Bengal, India, 2007
University of Windsor, M.A.Sc., Windsor, Ontario, Canada, 2009
University of Windsor, Ph.D., Windsor, Ontario, Canada, 2014