A Lithium-ion Test Cell for Characterization of Electrode Materials and Solid Electrolyte Interphase

Ekta Goel

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A LITHIUM-ION TEST CELL FOR CHARACTERIZATION OF ELECTRODE MATERIALS AND SOLID ELECTROLYTE INTERPHASE

By

Ekta Goel

A Thesis
Submitted to the Faculty of Mississippi State University in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry in the Department of Chemistry

Mississippi State University

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A LITHIUM-ION TEST CELL FOR CHARACTERIZATION OF ELECTRODE
MATERIALS AND SOLID ELECTROLYTE INTERPHASE

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The research discussed is divided into two parts. The first part discusses the background work involved in preparation of the Li-ion cell testing stage. This includes the preparation of anodes using the doctor blade and a calendar mill, electrolyte preparation, test cell assembly, the Li-ion test cell design, and experiments performed to troubleshoot the cell.

The second part deals with the cell testing experiments. Li-ion batteries are amongst the most promising rechargeable battery technology because of their high capacity and low weight. Current research aims at improving the anode quality to increase the capacity. The experiments discussed evaluate the traditional anode materials
like SFG44 graphite and conducting grade graphite against the novel ones— and tin oxide ($\text{SnO}_2$) based and carbon encapsulated tin based anodes. The solid electrolyte interphase formed on each anode was analyzed to understand the initial capacity fade leading to conditioning of the cell thus stabilizing its performance.

Keywords: Lithium-ion battery, anode material, solid electrolyte interphase, scanning electron microscopy
DEDICATION

I would like to dedicate this research to my mom and my brother - Ashish Goel.
ACKNOWLEDGEMENTS

This is perhaps the easiest and the hardest chapter that I have to write. It will be simple to name all the people who helped to get this done, but it will be tough to thank them enough. I will nonetheless try…

My utmost gratitude goes to my thesis advisor, Dr. David Wipf for allowing me to join his team, for his expertise, kindness, and most of all, for his patience. My thanks and appreciation goes to my thesis committee members, Dr. Alicia Beatty and Dr. Steven Gwaltney.

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Finally, and most importantly, I would like to thank the almighty God, for it is under his grace that we live, learn and flourish.
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<th>Description</th>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>EODV</td>
<td>End of discharge voltage</td>
</tr>
<tr>
<td>MPV</td>
<td>Mid point voltage</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>DMC</td>
<td>Di methyl carbonate</td>
</tr>
<tr>
<td>EMC</td>
<td>Ethyl methyl carbonate</td>
</tr>
<tr>
<td>VC</td>
<td>Vinylene carbonate</td>
</tr>
<tr>
<td>LI-GIC</td>
<td>Lithium-graphite intercalation</td>
</tr>
<tr>
<td>MCMB</td>
<td>Micro carbon micro bead</td>
</tr>
<tr>
<td>MCF</td>
<td>Micro carbon fiber</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl pyrrolidene</td>
</tr>
<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
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<tr>
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EDS  Electron diffraction spectrum
RE   Reference electrode
AE   Auxiliary electrode
CE   Counter electrode
WE   Working electrode
CRT  Cathode ray tube
MCA  Multi-channel analyzer
LIST OF SYMBOLS

$\Delta G^\circ$ = change in free energy

$n$ = number of electrons

$E^\circ$ = Standard electromotive force

$E$ = Voltage of the cell

$R$ = Universal gas constant

$F$ = Faraday constant

$T$ = temperature on absolute scale

$a^a_A$ = activity of reactant A

$a^b_B$ = activity of reactant B

$a^c_C$ = activity of product C

$a^d_D$ = activity of product D

$i$ = current flowing through the cell

$R_i$ = internal resistance of the cell

$(\eta_{a})_a$ = activation polarization at anode

$(\eta_{c})_c$ = activation polarization at cathode

$(\eta_{a})_a$ = concentration polarization at anode

$(\eta_{c})_c$ = concentration polarization at cathode

$i_0$ = exchange current density
$V_{SEI} = \text{voltage of SEI formation}$
CHAPTER I

INTRODUCTION

1.1 Introduction

Rechargeable Li-ion batteries have gained enormous attention because of their immense use in portable electronics like laptop computers and cell phones. The decreased size of electronic devices calls for the fabrication of small, light-weight batteries with long run times. Lithium-ion batteries, with high specific energies and long shelf life show a great potential to meet the current consumer demands. Current research is focused on improving the reliability, safety, and cycle life of Li-ion cells, which need further work.\textsuperscript{1-4}

The pioneering work on Li-based batteries was published by Harris in 1958.\textsuperscript{5} Eventually, further work led to the production of primary Li cells in 1970s. The study of Li-ion conduction in solids was studied in presence of an electrolyte that led to the development of a secondary Li-ion cell.\textsuperscript{1} The first commercial cell was manufactured by Sony in the 1990s.\textsuperscript{6}
1.2 Fundamentals

An electrochemical cell can be defined as a device that converts chemical energy into electrical energy by means of a redox reaction. This reaction is irreversible in case of a primary or a single use cell. In a rechargeable or secondary battery, the electrochemical process can be reversed to bring the cell back its original state. A collection of cells in series or parallel forms a battery.\textsuperscript{7} Lithium-ion cells belong to the secondary cell category and their features will be discussed a little later. The performance of a cell or a battery is characterized by its voltage (volts, V), capacity (ampere-hours, Ah), specific energy (watt-hours/kilogram, Wh/kg), specific power (watts/kg, W/kg), self discharge (%/month), cycle life, and recharge rates.

1.3 Design

An electrochemical cell is a combination of an anode, electrolyte, separator, and cathode. The anode of the cell loses electrons and thus is oxidized during the electrochemical reaction. The cathode accepts these electrons and undergoes reduction. The electrolyte is the bridge aiding in the travel of charge between the two electrodes.\textsuperscript{7} The anode and the cathode of a cell are separated by a porous membrane that allows the charge to pass on either side but prevents the anode and the cathode from coming in contact with each other, thus preventing short circuiting within the cell. This transport of electrons from one part of the cell to other causes the generation of electricity. The electrodes of a secondary cell can be restored to a condition of substantially complete charge by passing a current to flow into the cell.\textsuperscript{8}
Lithium-ion cells are becoming popular for their use in secondary battery technology. A Li-ion cell consists of a cathode that is a source of Li ions and an anode sink. A cathode is generally a Li-rich transition-metal compound with high Li chemical potential to increase cell voltage. It not only should allow Li insertion/extraction reversibly but should undergo very little or no structural change during the entire process. The compound needs to be an excellent conductor of ions and electrons and be chemically stable over the entire potential range involving the Li-ion shuttling process. The anode is the host for the Li ions and should have the lattice structure to accommodate these ions in addition to possessing all the properties of the cathode.9,10

1.4 Intercalation Process

It is interesting to know that the concept of intercalation was introduced by the Chinese more than 2700 years ago.11 The Chinese calendar, based on the motions of the sun and the moon had 12 months in each year, numbered from one through twelve. Since the twelve months were 11 days short of a tropical year, an additional month called the leap month was inserted about every third year to ensure the calendar was in tune with the seasons. This leap month was called the “intercalary month” and was the oldest known example of intercalation structure available.12 A few examples of intercalation materials are graphite,13,14 layered silicates, and clays, of which graphite is the most extensively studied. In addition, the field of intercalation of Li into graphite15,16 has been explored profoundly. This section is focused on the intercalation of Li into graphite forming compounds of the formula Li\(_x\)C\(_6\) where ‘\(x\)’ ranges between zero and one.17 The following figures represent the operation of a typical Li-ion cell consisting of a
carbonaceous anode and a Li rich cathode. Figure 1.1 represents the Li-ion cell in its discharged state. An electrochemical reduction occurs at the positive electrode and an oxidation at the negative one. The term reduction is used for Li insertion and oxidation for Li extraction in these cells.\textsuperscript{18} The total discharge reaction can be given by:

\[
\text{Li}_x\text{C}_n \rightarrow x\text{Li}^+ + \text{C}_n + xe^- \quad (1.1)
\]

During discharge:

Fig. 1.1 A Li-ion cell in a discharged state would appear like shown in the figure. Figure reproduced from reference [20].

The charging process illustrated in Figure 1.2 represents an opposite reaction wherein Li-ion de-intercalation occurs. The electrons are supplied by an external power
supply while the Li-ions travel from the positive to the negative electrode.\textsuperscript{20} The charge reaction can be given by:

\[ x\text{Li}^+ + C_n + xe^- \rightarrow \text{Li}_xC_n^{19} \]  

(1.2)

Fig. 1.2 A Li-ion cell in a charged state would appear as shown in the figure above. The figure is reproduced from reference [20].

The electrolyte used is ionically conductive and electronically non-conductive. Thus, the movement of Li-ions causes the flow of current and this behavior is generally termed as “Rocking-Chair” model of Li-ion battery. Additionally, this mechanism of operation makes the battery safer and less reactive chemically as it eliminates Li metal and the risks associated with it completely.\textsuperscript{7}
1.5 Defining Battery Performance

Various electrical and mechanical attributes define a battery performance. It is important to understand these parameters to evaluate the performance of a rechargeable battery. This section provides a brief review of battery performance.

A cell consists of two primary reaction sites – the cathode and the anode interface. The overall reaction that occurs at these interfaces determines the maximum electric energy that a cell can deliver. Thermodynamically, the change in free energy ($\Delta G^\circ$) of the electrochemical couple drives the cell to store/produce the electrical energy. This can be represented by equation 1.3:

$$\Delta G^\circ = -nFE^\circ$$  \hspace{1cm} (1.3)

where $F$ is the Faraday constant (96,487 coulombs/equivalent), $E^\circ$ is the standard potential and $n$ is the number of electrons. However, the above equation is applicable only under standard conditions of temperature and pressure. In other conditions, the Nernst equation (eq. 1.4) is used to determine the cell voltage ($E$).

Equation—

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a^c_c a^d_d}{a^a_A a^b_B}$$  \hspace{1cm} (1.4)

where $R$ is the universal gas constant, $T$ is the temperature on absolute scale, $a^a_A$ and $a^b_B$ are the activity of reactants and $a^c_c$ and $a^d_d$ are the activity of the products.

It is not possible to measure an absolute electrode potential. Therefore, H$_2$/H$^+$ is taken as ‘zero’ potential and all other half-cell reaction potentials are measured with respect to hydrogen electrode.
Theoretically, the available electrical energy is directly proportional to the amount of chemical energy stored on the electrodes. However, when a current ‘i’ is applied to the cell, the electrochemical reaction is accompanied with two kinds of polarization:

1) **Activation polarization**: Maximum driving force required to trigger the electrochemical reaction.

2) **Concentration polarization**: Since the reactants and the products are at different concentrations in the beginning, a concentration gradient develops from mass transfer limitations. This effect is called concentration polarization.

Another kind of polarization in addition to the above two is commonly observed – ohmic polarization. This is also called iR drop and is a result of the internal resistance of the cell which is the sum of the resistance of all the components that comprise the cell – the electrolyte, the separator, the current collectors, and the electrodes itself. The effect of this polarization can be represented in an equation using Ohm’s law. A cell voltage \( E \) in presence of an external load \( R \) is given by the following equation (eq. 1.5):

\[
E = E_0 - [(\eta_{ct})_a + (\eta_{ct})_c] - [(\eta_{ct})_c + (\eta_{ct})_a] - iR_i = iR
\]  

(1.5)

where \( E_0 \) is the electromotive force of the cell, \( R_i \) is the internal resistance of the cell, \( \eta \) is the overpotential, which may be due to activation or concentration polarization, and \( i \) is the current applied to the cell. The \( (\eta_{ct})_a \) and \( (\eta_{ct})_c \) are the activation polarizations at anode and cathode and \( (\eta_{ct})_a \) and \( (\eta_{ct})_c \) are the concentration polarizations at anode and cathode. This equation can be represented graphically as follows.
The cell voltage $E$ is defined as the potential difference across the cell terminals under zero load conditions. In other words, it represents the maximum ability of a cell to convert its chemical energy into electrical energy. However, in a practical cell, the energy loss is significant due to different polarization effects. The above plot is known as polarization curve and it illustrates the decrease in maximum deliverable voltage of a cell as a function of current. A desirable practical cell would be the one with minimal energy losses and the operating voltage close in magnitude to the open circuit voltage. The design parameters discussed earlier aid in minimizing the losses due to charge transfer reaction and diffusion rates. A Li-ion battery can have a maximum voltage of 4 V, which makes it amongst one of the most energetic batteries available today.

The other parameters that characterize a battery are capacity, energy, and power. These quantities can be represented in terms of specific values – per mass or specific...
densities – per volume. The theoretical specific capacity is defined as the amount of electricity generated by the electrochemical reaction based on anode and cathode active materials. The actual specific capacity that is used in practical considerations is the total electricity based on cathode, anode, and the inactive materials that are a part of the cell – the electrolyte, separator, and the current collectors. The units of capacity are Ah/kg. This value represents the number of amp-hours that a cell could store and deliver per kilogram of active material. A Li-ion battery marked as 1000 mAh will nominally generate a 1000 mA of current for one hour before it is completely discharged. The specific energy, expressed in Wh/kg is the total amount of electrical energy stored per unit weight of the cell. It is the multiple of capacity of a cell and its voltage. The specific power is a term that describes the rate at which this energy can be delivered. The units of specific power are W/kg.

The capacity of a cell is affected by a variety of factors that include the storage time, temperature, operating conditions, discharge current, and cell design. The discharge rate of a cell has a significant effect on cell capacity. A higher discharge rate can lower the capacity greatly. The following figure represents the decrease in capacity of a battery as the discharge current is increased.
The rate at which a cell is charged or discharged is denoted by the term called ‘C-rate’ of a cell. For example, a C/5 rate signifies that a particular cell will be charged or discharged to its actual capacity in 5 h. The same C-rate must be used when comparing two or more cells. Understanding cell performance parameters is the key to understanding the importance of Li-ion battery technology. The most important secondary battery technologies available today include Li polymer, nickel-cadmium, nickel metal hydride, lead acid, zinc/air and Li-sulfur batteries. The following table discusses the materials used in construction of each of these systems.
Table 1.1 Table listing the components of various different kinds of battery technologies available today. Table reproduced from reference [2].

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>Electrolyte, Separator</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium-ion</td>
<td>Carbon (graphite)</td>
<td>LiPF$_6$ in carbonate mixtures, Polypropylene</td>
<td>LiCoO$_2$</td>
</tr>
<tr>
<td>Lithium polymer</td>
<td>Lithium</td>
<td>LiN(CF$_3$SO$_2$) in PEO</td>
<td>LiV$<em>6$O$</em>{13}$</td>
</tr>
<tr>
<td>Nickel-Cadmium</td>
<td>Cadmium</td>
<td>Aqueous KOH, polypropylene</td>
<td>Nickel oxyhydroxide</td>
</tr>
<tr>
<td>Nickel Metal-hydride</td>
<td>Metal hydride</td>
<td>Aqueous KOH, polypropylene</td>
<td>Nickel oxyhydroxide</td>
</tr>
<tr>
<td>Lead Acid</td>
<td>Lead Alloy</td>
<td>Aqueous H$_2$SO$_4$, polyethylene</td>
<td>Lead dioxide</td>
</tr>
<tr>
<td>Zinc/Air</td>
<td>Zinc</td>
<td>Aqueous KOH</td>
<td>Carbon</td>
</tr>
<tr>
<td>Lithium-sulfur</td>
<td>Lithium</td>
<td></td>
<td>Sulfur, Carbon</td>
</tr>
</tbody>
</table>

As can be seen from the table, the materials used in various cells are different and this determines their individual performances. The following table (table 1.2) compares the performance characteristics of these secondary batteries. It is important to note that the values given in the table correspond to a representative design of the cell and will differ if the cathode, anode, or electrolyte is altered.
Table 1.2  Table showing performance characteristics of various Li-based cells. Table adapted from reference [2].

<table>
<thead>
<tr>
<th></th>
<th>Nominal Voltage (V)</th>
<th>Specific Energy (Wh/kg)</th>
<th>Energy Density (Wh/L)</th>
<th>Specific Power (W/kg)</th>
<th>Power Density (W/L)</th>
<th>Cycle Life</th>
<th>Self Discharge (%/month)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-ion</td>
<td>3.6</td>
<td>115</td>
<td>260</td>
<td>200-250</td>
<td>400-500</td>
<td>500-1000</td>
<td>5-10</td>
</tr>
<tr>
<td>Li polymer</td>
<td>3.0</td>
<td>100-200</td>
<td>150-350</td>
<td>&gt;200</td>
<td>&gt;350</td>
<td>200-1000</td>
<td>~1</td>
</tr>
<tr>
<td>Lead Acid</td>
<td>2.0</td>
<td>35</td>
<td>70</td>
<td>~200</td>
<td>~400</td>
<td>250-500</td>
<td>4-8</td>
</tr>
<tr>
<td>Ni-Cd</td>
<td>40-60</td>
<td>60-100</td>
<td>140-200</td>
<td>220-360</td>
<td></td>
<td>300-700</td>
<td>10-20</td>
</tr>
<tr>
<td>NiMH</td>
<td>60</td>
<td>220</td>
<td>130</td>
<td>475</td>
<td></td>
<td>300-600</td>
<td>30</td>
</tr>
<tr>
<td>Zn/Air</td>
<td>150</td>
<td>200</td>
<td>150</td>
<td>190</td>
<td>~200</td>
<td>~200</td>
<td>~5</td>
</tr>
<tr>
<td>Li-S</td>
<td>2.1</td>
<td>300</td>
<td>400</td>
<td>750</td>
<td>&gt;500</td>
<td>&gt;500</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

It is evident from the above table that Li-based cells have the highest specific energy and lowest self-discharge. Lithium, with its low weight delivers high voltage and superior performance. However, while designing these batteries for domestic applications safety becomes an extremely important concern. The electrolyte used in a battery is generally an organic liquid and it presents a danger of leakage, corrosion and sometimes explosion. Recently, Sony had to recall batteries used in laptop computers and in cell phones. The factors responsible for the explosions are discussed in Chapter two.
Another thing that can damage the cell is the way it is charged. Charging at a high rate might cause incomplete charging to occur leading to lower capacity. Charging the cell to the right voltage is important. Overcharging of the cell may result in electrolyte decomposition, build up of pressure inside the cell, reversing of electrode polarity or deposition of metallic Li on the carbon surface. Another aspect of charging, generally not seen in Li-based cell is called the ‘memory effect’. The memory effect is the irreversible loss of capacity seen during the subsequent cycles if the previous cycles of discharge were incomplete. Nickel-cadmium cells are known to suffer these effects and thus a complete discharge of the cell becomes essential before each cycle. The reason for the memory effects is attributed to large crystal growth that causes a voltage drop and a decrease in capacity.25

1.6 Ideal Charge/Discharge Curve

![Ideal Charge/Discharge Curve](image)

Fig. 1.5 A typical charge/discharge curve of a Rechargeable System. Figure reprinted from reference [28].
An ideal charge/discharge profile should be completely flat as shown in Figure 1.5. The discharge process should occur at the theoretical voltage of the battery until the active materials are utilized and then the voltage must drop to zero. During the charge, the voltage increase with time should be continuous until the theoretical voltage is reached i.e. until all the activity of the anode is restored. The point at which the discharge of a cell is said to be complete is known as the end of discharge voltage (EODV). The point in between the charging and the discharging voltage extremes is the mid point voltage (MPV). However, as discussed earlier, the operating voltage of a battery is lower than the theoretical voltage due to $iR$ losses. These losses even cause their charge/discharge profiles to be different than ideal. As a result, not only the operating voltage of the battery is low, but the initial power drain experienced by the battery when the discharge begins is high. This causes a sharp decrease in voltage. However, after the initial drop, the voltage profile remains considerably flat until the EODV is reached. The charge profile follows the same process in a direction opposite to discharge. Thus, the charge/discharge characteristics of Li-ion cell are the closest to the ideal profile and this gives another reason for industries to exploit the technology.

1.7 The Li-ion cell

Since their inception, Li-ion cells have undergone a variety of changes in terms of the materials used and their applications. The search for more efficient and safe anode, cathode, and electrolytes for use in the cell has been the major area of research. This
section is a brief overview about the battery materials, the methods commonly used in their development and the areas that need improvement.

### 1.7.1 Electrolyte

The main objective of an electrolyte is to provide an effortless conduction of Li ions and aid in the formation of a stable solid electrolyte interface (SEI) on anode layer. An ideal electrolyte should not only provide ease of transmission of ions in order to minimize cell resistance and thus lower the resistive heating of the electrochemical cell but should also be electrochemically stable over a broad voltage range. Additionally, it should have a low freezing point to avoid solidification at low temperatures and a high boiling point to avoid an unstable increase of pressure inside the cells. Lastly, it should be affordable and non-toxic in order to make its handling and disposing easy.

The electrolytes available for use in Li-ion batteries do not meet all the requirements of an ideal electrolyte. Certain combinations of electrolytes available today cannot be used at all temperatures while others are electrochemically unstable at the desired voltage range. However, the electrolyte conductivity and its stability are considered to be the primary parameters when evaluating electrolyte performance.

An electrolyte of Li-ion battery consists of a Li salt dissolved in a high purity non-aqueous organic electrolyte solution. The properties of non-aqueous electrolytes and Li salts have been extensively researched over the past 20 years. Non-aqueous electrolytes, consisting of organic carbonates are recommended materials for use in Li-ion batteries. The cyclic carbonates have high viscosity and the linear ones provide high fluidity. A mixture will yield an electrolyte with high ionic conductivity. Table 1.4 lists...
the ways in which the electrolyte solutions are combined with the salt to yield a better performing electrolyte solution. The salt concentrations used vary from 0.4 M to 1 M LiPF$_6$ and the temperature range is -40 to 50 °C. A salt concentration of less than 0.4 M is not practical because of its low conductivity. A concentration above 1 M is associated with precipitation and hence would be detrimental to the electrochemical cell. The temperature change is chosen based on the most common operating conditions of practical Li-ion batteries.

Electrochemical stability is a major concern in battery research as the reactions that occur on the surface of the electrodes are complex and diverse. Organic electrolytes tend to decompose at the negative electrode as they are incapable of tolerating the reducing power of metallic Li or Li-doped graphite. However, the stability of modern battery systems is based on the formation of a stable film called solid electrolyte interface (SEI) by the decomposition of organic solvents. The film formation and its properties will be discussed in detail a little later. It is important to know that this film prevents further decomposition of electrolyte and stabilizes the battery system protecting the anode layer.

The aim of much research has been to find carbonates that are stable above 4 V. Interestingly, the carbonates have shown remarkable stability exceeding 5 V, which makes their use in battery applications involving high operating voltages indispensable. The following table lists the oxidation potentials of various organic carbonates that are widely used in Li-ion battery applications.\textsuperscript{36, 37}
Table 1.3  Table showing the oxidation potentials of organic carbonates used in Li-ion batteries. Table adapted from reference [38, 39].

<table>
<thead>
<tr>
<th>Electrolyte Solvent</th>
<th>Oxidation potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene carbonate (PC)</td>
<td>4.3</td>
</tr>
<tr>
<td>Ethylene carbonate (EC)</td>
<td>5.2</td>
</tr>
<tr>
<td>Dimethyl carbonate (DMC)</td>
<td>5.1</td>
</tr>
<tr>
<td>Diethyl carbonate (DEC)</td>
<td>5.2</td>
</tr>
<tr>
<td>Methyl ethyl carbonate (MEC)</td>
<td>5.2</td>
</tr>
<tr>
<td>Gamma-butyrolactone</td>
<td>5.2</td>
</tr>
<tr>
<td>Diethoxyethane</td>
<td>4.5</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>4.1</td>
</tr>
<tr>
<td>2-methyltetrahydrofuran</td>
<td>4.3</td>
</tr>
<tr>
<td>1,3 dioxolane</td>
<td>4.2</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>3.8</td>
</tr>
</tbody>
</table>

In addition to the electrolyte systems discussed above, various kinds of substituted alkyl carbonate solvents like trans butylene carbonate were found to improve the reversibility of intercalation of Li ions into graphite by increasing the stability of SEI formed.\(^{38}\) Chlorinated and fluorinated alkyl carbonates are increasingly replacing EC, whose melting point is too high (room temperature).\(^{39, 40}\) The formation of SEI is known as the passivation of the anode. It is desirable to have electrolytes that enhance passivation. The use of alkyl, aryl, and allyl sulfites,\(^{41}\) alkyl nitrates,\(^{42}\) sulfates,\(^{43}\) and phosphonates\(^{44}\) as co-solvents has been suggested to increase passivation and decrease irreversible capacity loss. Another additive, vinylene carbonate (VC), is increasingly gaining importance due to its higher reactivity compared to EC, and its ability to form
polycarbonates on LiMO₉ cathodes. Also, VC is shown to increase stability of the system at elevated temperatures and decrease irreversible capacity.⁴⁵ Alkyl phosphates and phosphazenes are considered non-flammable,⁴⁶ with phosphates having the added advantage of stabilizing LiPF₆.⁴⁷ Biphenyls are believed to protect the system against overcharging.⁴⁸ An active gas like CO₂ is an exceptionally good passivating agent.⁴⁹ It forms Li₂CO₃ on Li-C surface and thus could be used as an additive. Similarly, SO₂ forms Li₂S, Li₂SO₃, Li₂S₂O₄, and Li₂O leading to excellent passivation of carbon anode.⁵⁰

Table 1.4 Table of solvents and electrolytes used in Li-ion batteries. LiPF₆ is the salt used with the list of electrolyte mixtures. Table adapted from reference [1].

<table>
<thead>
<tr>
<th>EC</th>
<th>DEC</th>
<th>DMC</th>
<th>PC</th>
<th>EMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>DEC</td>
<td>DMC:EC</td>
<td>PC</td>
<td>EMC</td>
</tr>
<tr>
<td>EC:DEC</td>
<td>DEC:EC</td>
<td>DMC:DEC</td>
<td>PC:DEC</td>
<td>EMC:EC</td>
</tr>
<tr>
<td>EC:DMC</td>
<td>DEC:PC</td>
<td>DMC</td>
<td>PC:DMC</td>
<td>EMC:PC</td>
</tr>
</tbody>
</table>

As suggested earlier, binary solvents i.e. the solvents formed by mixing two carbonates are better than single solvents. The most common binary solvents are based on EC-DMC or EC-DEC systems. They provide a wide temperature range of -40 to 50 °C and possess remarkable conductivity when compared to the single electrolyte solvents. Another level of hierarchy is added by combining three carbonates such as PC-EC-DMC which provide higher conductivity over binary solvents. The added benefit is that the salt consumption is reduced, which reduces the cost of the battery. The temperature range offered is similar to the binary solvents.
In addition to electrolyte solvent, the salt used has been an important arena of recent research related to Li-ion batteries. Thermal stability is an issue with LiPF$_6$. Recently, Merck introduced LiPF$_3$(CF$_2$CF$_3$)$_3$(LiFAP), a salt proven to be of higher stability and less acidic than LiPF$_6$. $^{51}$ Another salt LiN(SO$_2$CF$_2$CF$_3$)(BETI) was introduced but was found to behave poorly when compared to LiPF$_6$ or LiFAP salts.$^{52}$ Another salt seeking approval to replace LiPF$_6$ is ‘LiBOB’, Libis(oxalo)borate salt.$^{53}$ It has shown high reversibility but research is still in progress to establish its credibility. The organic electrolytes have been found to be unstable on standing.$^{54}$ They undergo reactions leading to formation of transesterification products due to presence of acidic impurities. Also, ethylene carbonate is capable of undergoing polymerization leading to production of CO$_2$ gas.$^{55}$ These undesirable reactions force researchers to view alternatives like polymer electrolytes that are not only non-volatile but could also prevent the runaway reactions.$^{56}$ Polyelectrolyte membrane (PEM), as it is called is gaining interest to assist in the development of Li metal polymer battery systems. However, the research is still primitive and needs tremendous molecular modeling and other diagnostics techniques in order to be able to synthesize usable membrane.$^{57}$

In sum, this section discussed the present research dedicated towards finding efficient electrolytes that can be used in Li-ion batteries. An ideal electrolyte would be electrochemically stable at a wide voltage range, have thermal stability to be functional at temperature extremes and would have high ionic conductivity. A mixture of organic solvents in various ratios produces an electrolyte with properties close to the ideal one.
1.7.2 Anode

Carbonaceous materials, particularly graphite have been popular candidate materials for anode because of their low cost, good reversibility, and safe disposal. Graphite consists of sp\(^2\) hybridized carbon atoms as hexagonal graphene sheets. These sheets are stacked into an ABAB… sequence along the C-axis. The space group that this lattice is a part of is P6\(_3\)/mmc with the a- and c-axis lengths of hexagonal unit cell being \(a_0=0.246\) nm and \(c_0=0.6708\) nm. As is evident from the picture, graphite has two surfaces, a basal plane and an edge plane. The basal plane is the plane orthogonal to the c-axis, visible and the edge plane is the one parallel to the c-axis.\(^5\)

![Crystal Structure of Graphite](image.png)

Fig. 1.6 Crystal Structure of Graphite showing the ABAB…stacking sequence. Reprinted from reference [60].
The structure of graphite is critical to the understanding of intercalation/de-intercalation mechanism. The intercalation of Li ion with graphite forms Li-graphite intercalation compounds (Li-GICs).\textsuperscript{59, 60} The Li-GICs formation occurs in a series of steps known as the staging process. This mechanism has been studied using X-ray diffraction\textsuperscript{59, 60} and Raman spectroscopy.\textsuperscript{61-63} As the voltage decreases, the staging process proceeds from a higher to a lower stage. De-intercalation occurs in the exact opposite direction. The following equations (eq. 1.6 through 1.8) represent the stage changes and their corresponding voltages.

\begin{align*}
\text{Dilute stage-1} & \rightleftharpoons \text{Stage-4 (ca. 210 mV)} \quad (1.6) \\
\text{Stage-2L} & \rightleftharpoons \text{Stage-2 (ca. 120 mV)} \quad (1.7) \\
\text{Stage-2} & \rightleftharpoons \text{Stage-1 (ca. 90mV)} \quad (1.8)
\end{align*}

The dilute stage refers to a random graphite-Li intercalation. The letter L in the second equation suggests the liquid-like stage-2 where there is no in-plane ordering. The following is the schematic diagram of the stages of intercalation. The GIC formation is said to be complete at the end of Stage-1. At this stage, the Li-GIC forms a “super lattice” (as seen in Figure 1.7) where the Li is characterized by a $\sqrt{3} \times \sqrt{3}$ structure.\textsuperscript{64} This structure is the key to the LiC$_6$ composition of Li-GICs.
Cyclic voltammetry and charge/discharge experiments have been performed to study the staging process using various kinds of natural and commercially available graphites.\textsuperscript{3, 65-68} Wang et al.\textsuperscript{69} conducted cyclic voltammetry experiments and charge/discharge experiments on natural graphite and a variant to determine the rate capability of graphite electrodes. The cyclic voltammogram shown in Figure 1.8 was obtained at the scan rate of 0.2 mV/s. The anode was made with 90 \% weight natural graphite and 10 \% by weight PVDF binder dissolved in NMP. The electrolyte used was 1 M solution of LiPF\textsubscript{6} dissolved in ethylene carbonate, diethyl carbonate, and propylene carbonate in various ratios. As can be seen in the voltammogram, the cathodic peaks corresponding to SEI formation occur in the range of 0.9 to 0.1 V. These values represent the normal range for a variety of graphites. The solid line represents the first cycle and the dotted line represents the second cycle of experiments.
In addition to the cyclic voltammetry curves, the initial charge/discharge curves were plotted as shown in Figure 1.9. As can be seen in the graph, the plateaus represent the intercalation phenomenon of Li into graphite. As discussed, the intercalation of Li into graphite proceeds in four different stages. Each stage is represented by a number and the intercalation is said to be complete when the Li-graphite intercalation compound (Li-GIC) is formed. The voltage range 0.9-0.6 V is typical for the intercalation to occur. Nonetheless, this voltage could vary based on the type of graphite used to fabricate the anode.
Fig. 1.9 Charge/discharge curve of natural graphite showing the plateaus for Li-ion intercalation into graphite. Figure reprinted from reference [71].

Graphite is available as MCMB (mesocarbon microbeads), MCF (micro carbon fiber) or just natural and synthetic graphite flakes. MCMB material is associated with the highest capacity but is expensive.\textsuperscript{62, 70, 71} Buqa et al.\textsuperscript{72} conducted experiments on three different graphites – SFG44, SFG15 and SFG6 to compare the irreversible loss in capacity during the first couple of cycles. The effect of particle size of graphite and the charge rate on the irreversible capacity loss were analyzed. Apparently, both these factors have a significant effect on the SEI formation. Figure 1.10 shows their data at different scan rates. Since SFG44 graphite has the largest particle size, it shows rather low rate capability. At 1 C rate, less than 50% of its specific charge capacity is obtained. For smaller particles of SFG15 and SFG6, the capacity is higher in comparison. The particle size thus affects the quality of SEI formed on the surface. According to Ning et al.,\textsuperscript{73} the greater particle size of graphite accumulates more Li. High Li concentration along with
high current density on these particles causes a quicker formation of SEI. Nonetheless, the SEI formed is non-uniform, has defects (cracks) and is thick. The SEI on smaller particles is less dense and more uniform. Thus, the SEI formation is related to the initial loss in irreversible capacity of the anodes.

![Graph showing capacity graph of SFG44, SFG15, and SFG6 graphite with respect to the cycle number.](image)

**Fig. 1.10** Capacity graph of SFG44, SFG15, and SFG6 graphite with respect to the cycle number. Figure reprinted from reference [74].

In studies conducted by Booth et al., three generations of graphites were evaluated for capacity loss due to SEI formation. Their studies involved synthetic graphites like mesophase carbon microbeads (MCMB), carbon fiber, and natural graphite. The data obtained for the initial charge/discharge curve at C/20 rate is shown in Figure 1.11. The natural graphite and MCMB have a similar behavior while the hard carbon has a completely different curve. Hard carbons have a crystalline structure.
and limited lattice organization. Thus, their charge/discharge curves do not show any plateaus for staging. The intercalation of Li proceeds by filling any of the available sites that might cause the capacity of hard carbons to be higher than the natural graphite. However, in the experiments performed by Booth et al., this phenomenon was not observed.

The natural graphite and the MCMB graphs showed distinct plateaus representing the staging phenomenon of graphite. The first plateau at 0.2 V vs. Li corresponds to stage IV. As we might recall, during this stage there are four graphene layers that separated two layers of intercalated Li. The peaks close to 90 mV show stages II and III. The stage I correspond to the formation of LiC₆ and is seen below 50 mV.

Fig. 1.11 Galvanostatic charge/discharge curve of hard carbon, natural graphite and MCMB obtained at C/20 rate. Figure reprinted from reference [67].
Along with carbon, members of Group III and V elements like Al, Si, Ge, Sn, Pb, Sb, and Bi, are capable of forming alloys with Li and are considered as active materials. Tin is the most popular of all these and the studies show the existence of seven phases of Li-Sn system-Li$_2$Sn$_5$, LiSn, Li$_7$Sn$_3$, Li$_5$Sn$_2$, Li$_{13}$Sn$_5$, Li$_7$Sn$_2$, and Li$_{22}$Sn$_5$. However, recent studies have shown excellent reversibility based on alloying between the Li with the Sn centers in tin oxide composites that give rise to Li$_{4.4}$Sn nanoparticles.

Antimony exhibits considerably good capacities owing to alloying reactions with Li, just like tin. The alloying reactions result in formation of Li$_3$Sb with a theoretical capacity of 660 mAh/g. In a study by Thackeray et al., a novel Li-insertion compound was proposed. A Li-insertion compound is a host material that has the ability to reversibly and topotactically intercalate Li. Alloying and de-alloying leaves the host material with expanded volumes. This drawback is effectively eliminated in Li-insertion hosts. The most common type of host materials are copper/tin systems like ηCu$_6$Sn$_5$, InSb, and SnSb systems. Metal oxides are widely considered due to their ability to intercalate at very low potentials. TiO$_2$, in its anastase polymorph form and TiO$_2$(B) produced by ‘chimie douce’ procedures are most common metal oxides where insertion is the key to electrochemical efficiency.

In addition to the above systems, various futile efforts have been made to determine the properties of aluminides and silicides as potential candidates for anodes in Li-ion batteries. Nitrides, of the formula Zn$_3$N$_2$ undergo a complex reaction leading to the formation of LiZn in a matrix of β-Li$_3$N giving a reversible capacity of 555 mAh/g. These compounds are limited by their cyclability but are currently under investigation as a promising anode material. Phosphides, like nitrides and antimonides are gaining interest.
as a negative electrode material because the MnP₄ compound acts as a reservoir for Li. Capacities of 550 mAh/g are observed for up to 25 cycles at a C/4 rate.⁹⁰

The above paragraphs provide an overview of different kinds of materials being investigated by various research groups to increase the capacity of Li-ion batteries. The graphitic form of carbon is still the most popular material and the other compounds can be used as additives to enhance the battery performance. In the study described in this thesis, the focus is on comparison of the most commonly used graphite material i.e. SFG44 with an enhanced version of graphite that is made commercially available for testing ‘conducting grade graphite’, a SnO₂-SFG44 graphite-based composite and a carbon nanotube encapsulated Sn-SFG44 graphite-based composite anodes.

1.7.3 Cathode³

The first battery introduced by Sony used a LiCoO₂ cathode⁹¹ and this material has been a popular choice since its release. The cathode of a cell is the source of Li-ions and hence its primary requisite is to have numerous sites for Li⁺. The cathode should be stable towards the electrolyte and should be capable of undergoing intercalation and de-intercalation reactions reversibly. Finally, it should be easy to fabricate with reproducibility and should be non toxic.

It is an established fact that ideal cathodes do not exist. However, scientists have been able to research many different cathodes with exceptionally good behavior. The following table lists the most widely used and researched cathode materials that have been reported over the past 15 years.
Table 1.5  Cathode materials of interest based on their voltage range. Table reprinted from reference [3].

<table>
<thead>
<tr>
<th>V Range</th>
<th>Typical Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>LiMn_{2-x}M_{x}O_{4} (x ≥ 0.5)</td>
</tr>
<tr>
<td>4</td>
<td>LiNiO_{2}, LiCo_{2}, LiCo_{1-x-y}O_{2}, LiMn_{2}O_{4}, Li_{1+x}Mn_{2}M_{y}O_{4} (low x and y)</td>
</tr>
<tr>
<td>4-3</td>
<td>LiMnO_{2}, Li_{x}Mn_{1-y}M_{y}O_{2}, Li[Li_{x}myMn_{1-x-y}]O_{2}</td>
</tr>
<tr>
<td>3.5</td>
<td>LiFePO_{4}</td>
</tr>
<tr>
<td>3</td>
<td>Mn Spinels, Li_{x}MnO_{2}, Li_{x}V_{y}O_{2}</td>
</tr>
<tr>
<td>2</td>
<td>S and Polysulfides</td>
</tr>
<tr>
<td>1</td>
<td>FeS_{2}</td>
</tr>
</tbody>
</table>

Synthesis of cathodes is an important area of research since they demand both purity and homogeneity. Additionally, the kind of cathode material desired is based on the route by which it is synthesized. The traditional process used is called ‘sol-gel’ wherein a cathode material like LiMn_{2}O_{4} is synthesized using adipic acid as chelating agent.\textsuperscript{92} Other techniques include combustion,\textsuperscript{93-96} reduction and oxidation procedures,\textsuperscript{97} ion-exchange,\textsuperscript{98} and hydrothermal synthesis.\textsuperscript{99-102} Recently novel techniques of synthesis like spray drying,\textsuperscript{103} emulsion drying,\textsuperscript{104} and freeze drying\textsuperscript{105} have been used to synthesize cathodes by suspending the precursors in aqueous solutions to form submicron sized particles. These techniques are rather complex and need further investigation before they can be used for commercial synthesis.

All the cathode materials mentioned in the table above have been studied well and are suitable for industrial purposes. LiCoO_{2} has been optimized to a particle size of 20
and has been made thermally stable by various types of coats.\textsuperscript{107, 108} Efforts are currently in progress to decrease its price to make the Li-ion system more affordable. The Ni- and Mn-based electrodes have been improved since their inception in terms of their cycle life\textsuperscript{109} and their low operating voltage.\textsuperscript{110, 111} However, these systems tend to occupy a limited share in the battery market owing to their low capacity when compared to LiCoO\textsubscript{2}. Nickel-based cathodes are becoming increasingly popular because they are relatively inexpensive and offer high and stable capacities when present with manganese\textsuperscript{112} or aluminum.\textsuperscript{113}

The cathode materials available today perform very well and the way research is being carried out in this arena will eventually lead to the development of more efficient layers.

\textbf{1.7.4 Separator}\textsuperscript{7}

The anode and cathode materials are physically separated by means of an ionically conducting grid structure called the separator. The material used as separator should be permeable to electrolyte and thus provide sufficient conductivity. Additionally, it should be of adequate thickness (10 to 30 µm) in order to decrease the electrolyte resistance and thus decreasing the $iR$ drop across the cell. Additionally, a separator should be easily wetted by the electrolyte and be stable when placed in contact with the electrode and electrolyte in a cell.

Separators have been an important area of research and the properties of commercially available separators have been reported.\textsuperscript{114} The commonly used separators in Li-ion batteries are micro-porous polyolefin based materials with pore size of less than
1 µm. These are synthesized from polyethylene or polypropylene or laminates of these compounds and coated for improving the wetting property by solvent based processes\textsuperscript{115}. These materials suffer from loss of porosity at their melting temperatures\textsuperscript{116}. Hence, a tri-layer design is considered with polyethylene sandwiched between two polypropylene layers – the polypropylene layer helps maintain the integrity of the film while polyethylene acts as a thermal fuse when the cell reaches undesirable temperatures.

In addition to the above components, a Li-ion cell is comprised of two current collectors that act as substrates to hold the electrode materials. These support the anode and cathode and provide a uniform current distribution along with low contact resistance to minimize the polarization of an electrode during the operation of the cell. Additionally, these are drafted from materials that are not prone to corrosion because this has been an important reason for battery failure\textsuperscript{117} in the past. The most common current collectors used are made of copper and steel.

### 1.8 Importance of SEI\textsuperscript{118}

The SEI can be best described as an interphase present between an electrolyte and the surface of the electrode that has the properties of a solid electrolyte.\textsuperscript{119} SEI formation is considered to be one of the most important reactions occurring in a Li-ion cell as it determines the safe and effective operation of the system. The SEI should be stable and highly permeable to ions. Additionally, it should be an electronic resistor to avoid any self discharge of the battery. It should be uniform and have good adhesion to the anode. This section focuses on SEI formation on carbonaceous electrodes and its importance.
As discussed earlier, graphite has hexagonal graphene sheets stacked together in an ABAB…sequence. A complicated set of reactions might occur when the Li intercalates with graphite for the first time. These reactions are schematically represented in the following figure.\textsuperscript{7,120} The desired reactions lead to the formation of SEI and the undesirable ones disrupt the graphite structure, leading to cell damage.

![Diagram of reactions](image)

**Fig. 1.12** Schematic representation of reactions occurring on carbon electrode. Figure redrawn from reference [22].
For the intercalation of Li ion to occur, the Li loses its solvation shell while penetrating through the SEI and thus sits inside the graphite that is free from solvent. The phenomenon of graphite entering Li in its solvation shell is thermodynamically less favorable. In addition, solvent does not prefer to get into the graphite sheets due to a repulsive interaction between graphite and solvent particles. Thus, there is no or very little motivation for solvated Li to intercalate between graphite layers. If, however, Li enters graphite with its salvation shell, it leads to disruption of graphite structure. In addition to the electrolyte and the Li ions, various other salts, solvents, and impurities compete for reduction reactions. Their rate depends upon their exchange current density ($i_0$) and the catalytic properties of carbon surface. The reduction reactions produce salt anions like LiF, LiCl, and Li$_2$O that precipitate on the surface of the anode. The solvent reduction, on the other hand, results in formation of insoluble polymers and salts like Li$_2$CO$_3$ on the SEI. Due to the difference in catalytic properties of different kinds of carbon, temperature, concentration of salts and impurities and current density, the SEI formation occurs at different voltages. For Li-ion batteries, the typical range of voltage leading to SEI formation ($V_{SEI}$) is 1.7 – 0.5 V vs. Li/Li$^+$.\textsuperscript{121} In some cases, the SEI formation is not complete in one charge/discharge cycle and may need several cycles until it is completely formed.\textsuperscript{122}

The SEI formation can be enhanced by pre-treatment of the surface of graphitic electrode materials by air-oxidation.\textsuperscript{120, 123, 124} The pre-treatment imparts nano-channels to graphite which aid in better bonding of SEI to the surface through carboxylic and oxide groups. This brings an overall increase in the reversible capacity of the cell and decreases the irreversible consumption of material and charge.
The chemical composition of SEI depends on the materials and morphology of carbon surface. The solvent and the salt forming the electrolyte play an important role in determining the SEI composition. Inaba et al. concluded that electrolyte combination consisting of EC:DEC yielded more stable SEI than EC:DME.\textsuperscript{125}

1.9 Summary

This chapter has described the basics of the Li-ion cell and the principles that govern its operation. It is important to understand this to be able to appreciate the work done in this project. The work described in the subsequent chapters explains the approach towards developing a laboratory scale test cell to be able to perform experiments. It provides a step by step guide to deal with the challenges that a researcher might encounter while in the process of setting up the instruments. Additionally, correct and the incorrect data are reported to point out the subtleties that might help distinguish right from wrong. An analysis of anode materials is done in order to compare their performance. Finally, the SEI characterization through scanning electron microscope is described and its characteristics and significance are explained.
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CHAPTER II
DEVELOPING THE CAPABILITY FOR ELECTROCHEMICAL TESTING OF
LI-ION CELL ELECTRODE MATERIALS

2.1 Introduction

Prior to the start of the work described here, no specific capability existed locally for electrochemical testing of candidate anode materials for Li-ion cells. As part of the collaborative research effort to develop improved anode materials, this research effort was geared toward developing the capability to perform electrochemical stability and capacity measurement of the materials. Thus, this chapter provides a detailed overview of the steps taken to implement testing of Li-ion cell materials. The research goal was to develop the ability to do short- and long-term testing of candidate materials specifically for Li-ion batteries. The Li-ion cell is an assembly of various materials, each of which requires processing and development. The following diagram is a pictorial representation of how an ideal cell for testing anode materials might be designed:
As shown in Figure 2.1, a typical cell would have a working electrode comprised of a copper foil supporting the anode material film, an auxiliary electrode, a reference electrode, a separator membrane for physically isolating the working electrode from the auxiliary electrode, a set of current collectors, and connectors to complete the circuitry. Note this cell is different than typical cell used in Li-ion battery in that the Li-metal oxide (e.g. LiCoO$_2$) is replaced with a Li metal electrode. This simplifies the cell and allows the behavior of the anode material to be studied in isolation. An ideal working electrode for a Li-ion cell consists of an extremely thin film of active material spread evenly on a supporting material. Copper metal foil has been traditionally used to provide the necessary support to the anode films.$^{2-6}$ A current collector is a material of high electric conductivity that enables the flow of current to and from an electrode during the
operation of a cell. Copper is an excellent conductor of electricity and thus is most suitable for use.

The anode film development on the copper is a challenging task requiring attention to a great amount of details. The composition, thickness and compression strength of the anode films are the quantitative parameters that are determined before it is made. These will be discussed in greater detail when dealing with the anode film development procedure. The purpose of the present section is to introduce the details that are considered before each component of a Li-ion cell is assembled. As already discussed, the anode active materials are the compounds that are capable of reversibly intercalating Li ions. A graphitic form of carbon has been most widely used to make battery anodes and this forms the primary anode active material in this research.

The next component of the cell in the figure is the auxiliary electrode. As we already know, the cathode of a Li-ion cell consists of a Li-rich compound that can act as a source of Li-ions and is capable of reversibly intercalating them. Additionally, like the anode, the cathode requires a current collector for establishing contact with the external circuit. The cathode and anode are physically separated by means of a porous separator membrane to prevent short circuiting. The reference electrode provides a standard measure of the potential difference across the cell. The connectors are used to complete the cell circuitry by establishing connections of the cell to the outside. Finally, room for electrolyte is required to aid in Li-ion conduction.

Thus, a cell design for a Li-ion cell testing would ideally represent the above skeleton. In addition to cell design, each individual component of the cell would require detailed research to ensure correct and optimum performance. The subsequent sections
will discuss the challenges and procedures developed during the research period. The major accomplishments achieved with respect to the research goal are enumerated below:

1. An inert atmosphere dry box has been set up.
2. A test cell was designed.
3. The battery testing potentiostat was obtained and programmed for efficient cell testing.
4. A standard procedure to make anode films was developed.
   (a) The anode composition was optimized.
   (b) A doctor blade was designed.
   (c) Compression of layers using a calendar roller mill was achieved
5. The cathode, reference electrode, separator, and electrolyte were standardized.
6. Test cell assembly was made.
7. The test cell and the cell materials were troubleshooted for functionality and reproducibility.
8. Miscellaneous issues with the experiments were successfully tackled.

2.2 Setting up an inert atmosphere dry box

Lithium is a highly reactive metal and is capable of undergoing fast oxidation reaction in presence of air. Thus, Li and Li-based compounds are obtained in sealed, argon-filled packages. Since the materials involved in Li-ion cell testing involve a variety of Li-based compounds, these require their storage and use in air-free atmospheres. The dry box or the glove box, as it is generally called, offers an argon-filled low oxygen and moisture atmosphere that is used to store and use Li metal and Li based salts.
The Li-ion cell, once assembled, is tested inside the box using the potentiostat present outside. To establish the connections from the atmosphere into the dry box, hermetically sealed electrical feedthroughs were installed on the wall of the dry box. The dry box was equipped with enough feedthroughs to perform testing of three half-cells simultaneously. In addition to storage and testing, the dry box was equipped with a balance, Kim-Wipes, volumetric flasks, glass slides, weighing paper, trash box, and disposable glass pipettes that are useful for procedures carried inside the dry box.

The transport of a material into the dry box might carry traces of oxygen and other moisture that might compromise the quality of the atmosphere inside it. Thus, the dry box atmosphere needs to be tested for oxygen and water content before use. In the present set up, titanium tetrachloride (Acros Organics, 99.9% purity) and a zinc chloride solution (Acros Organics) were used to test for the presence of oxygen and moisture respectively.

### 2.3 The Li-ion test cell

Figure 2.1 describes the internal framework of the Li-ion cell. The test cell design was based on the idea of encapsulating this framework. In addition to this requirement, the test cell design was also based on various other parameters.

**a. Material**

The test cell is basically an enclosure for the active materials of a Li-ion cell. Thus, the performance of the test materials can be accurately determined only if there were minimal or no side reactions. Thus, the body of the cell should be made of a completely non reactive material that does not interfere with the materials being tested.
b. **Electrical contacts**

From the description of Figure 2.1, it is learnt that the current collectors are crucial to completing the cell circuit. The current collector for anode film is copper. Aluminum has been used as the current collector for cathode. However, other metals capable of electric conductivity are equally desirable for use. These current collectors require connection to the external circuit by means of the electrical contacts present in the cell. Thus, the electrical contacts require that they are good conductors of electricity.

c. **Geometry**

The amount of flow of electric current is also dependent upon the surface area in contact. Thus, the connector should be so designed that its shape matches the shape of the corresponding electrode to achieve maximum contact and thus maximum current flow.

d. **Compression**

In addition to ensuring the contact between the electrode and the connector, it is important that there is a maximum contact between the cathode and the anode themselves. The idea of compression is to have a mechanism by which both the electrodes are pushed towards each other with certain minimal force that is just sufficient to place them against each other. Too much compression would lead to undesirable crushing of the electrodes. Hence, the design of the cell should incorporate a mechanism to establish maximum contact.
e. **Port for electrolyte**

The operation of the cell would require an uninterrupted supply of electrolyte. Thus, the cell would have to be made in a manner that it has a small place to hold some electrolyte solution that would last for the life of the experiment in progress. The solution could be refilled for the next set of experiments and this would make the cell reusable for the same set of materials.

f. **Port for reference electrode**

The reference electrode is required to be present to be able to measure the voltage difference across the circuit. It is important that the reference electrode is constantly in contact with the electrolyte for accurate readings. Thus, the design of the electrolyte and the reference electrode must be worked in conjunction in order to achieve the desirable reading.

g. **Versatility**

One of the most important parameters is the versatility of the cell. The current research focuses on Li-ion batteries and hence the cell design should be based primarily on the present area of importance. However, it is for the best to have a universal cell that could be used for testing other kinds of battery chemistries.

h. **Sealing**

In Li-ion cell testing, the materials are air sensitive. Hence, the cell should be so designed that it can seal the active materials hermetically and thus allows testing both outside and inside the dry box. This can attribute an additional dimension to the cell testing efficiency.
The cell should be designed in order to meet all the above requirements. A prototype cell was obtained from ABSL Ltd and the cell design was laid out based on this exemplary cell. The following figure is a photograph of the test cell and the visible parts are labeled. The cell body is made from high density polyethylene (HDPE). The metal parts are made from corrosion-resistant type 316 resistant stainless steel. A stainless steel compression spring is used to support the floating electrode inside the cell and to provide maximum contact between the electrodes.

![Photograph of Li-ion test cell](image)

Fig. 2.2 Photograph of Li-ion test cell.

The following figures are the schematic diagrams of the cell design and use the English (inches) system of units. Figure 2.3 represents the drawing of the outer body of the cell. The cell body is identical at both ends. It consists of a central groove to hold the metal electrodes. This groove is equipped with O-ring to prevent leakage. On the top, a
A wide cut is made to accommodate the fill port clamp. In this cut, a hole is drilled to accommodate the fill port. This port is meant to hold the electrolyte solution and the reference electrode.

Fig. 2.3  Schematic diagram of the cell test body.
Figures 2.4 and 2.5 show the schematic diagram of the anode of the test cell. The floating anode is the point of contact with the anode current collector. This short circular piece of metal is equipped with an O-ring to provide moisture lock inside the cell and also prevent electrolyte leakage. The floating anode is cupped to accommodate the spring that provides connection and compressibility to the anode connector (Figure 2.5). This connector has a banana type connector cup on the inside to accommodate the compression spring. The spring fits in between the cup of the floating anode and the anode connector. As already mentioned, the test cell design parameters require a compression mechanism to maximize contact between the anode and the cathode. The spring provides this mechanism efficiently as it pushes the floating anode towards the cathode.

Fig. 2.4   Schematic diagram of the Li-ion test cell floating anode.
Fig. 2.5  Schematic diagram of the Li-ion test cell anode.
Figure 2.6 illustrates the cathode contact of the Li-ion test cell. The electrode part is detachable from the cell with the help of a screw that goes into the triangular metal frame. The connector is a banana jack, like that of the anode. The connector fits snugly
into the cavity of the plastic body. This electrode is also supplied with an O-ring to provide moisture-lock.

Fig. 2.7 Schematic diagram of the electrolyte port of Li-ion cell.
Figure 2.7 represents the fill port of the test cell. It is a metallic tube with a tapered end. One half of the port is slid inside the plastic body while the remaining half is exposed to the outside. The part that fits inside the cavity is of smaller diameter than the part that is outside. The lower portion is meant to hold the electrolyte and the upper portion to hold the reference electrode in place. Figure 2.8 illustrates the stainless-steel clamp made of holes that holds the fill-port in place.

The cell design, though complicated is meant to provide easy operation of experiments. The parts of this test cell are removable and the screws and O-rings are replaceable. This accounts for more flexibility in operation. In sum, the most important criteria of the cell design have been addressed through this cell. As will be discussed later, some of the parts of the cell had not been utilized due to the impediments they posed to experiments.

Fig. 2.8  Schematic diagram of fill port clamp.
2.4 Potentiostat – Solartron 1470 E

The electrochemical test instrument used for the experiments is Solartron 1470 E (Solartron Analytical, Hampshire, England), a multichannel potentiostat unit. It provides various ranges and test conditions for batteries, fuel cells, super capacitors, and electrochemical cells. CellTest software is used to program the instrument. The 1470 E has eight main channels that provide the ability to simultaneously test eight cells of any kind. Each channel has an associated auxiliary channel that provides enhanced measurement details. Each main channel is capable of operating independently i.e. executing its own schedule without interfering with other channel. Additionally, more than one channel can be programmed to execute the same schedule. Each main channel cable has four electrode connections - Working Electrode (WE -), Counter Electrode (CE +), Positive Sense (RE1) and Negative Sense (RE2). These designations are only a standard for representing the cables and can be varied depending on the operating voltage required by the battery. In this project, the Li-ion cell assembled for tests had the reference electrode connected to the negative sense. The working electrode connector was joined to the Li auxiliary electrode of the cell. The counter electrode and the positive sense were joined together and connected to the carbonaceous anode. Figure 2.9 represents the actual connections made outside the dry box to the Solartron.
Once the connections were established, an experiment schedule was designed to perform cell testing. There are three common steps that can be included in a schedule:\(^\text{11}\)

1. Rest Step: A rest step measures the battery voltage under no load condition, which represents the open circuit voltage of the cell.
2. Normal Step: This step is used to set potentiostatic or galvanostatic charge/discharge conditions for a cell. The signals generated can be constant, ramp, square, and triangular pulses.
3. Loop step: This is used to create a schedule that runs more than once.

The schedule used for battery testing involved constant-current charging and discharging steps with rest steps at the beginning and at the end. Additionally, the loop
allowed repeating the schedules to collect more data. The actual schedules are defined for each experimental result.

2.5 Anode-Film Development

The anode forms the heart of the Li-ion cell and various factors must to be considered for its design. The anode of a Li-ion cell must be made from a material that is capable of reversible Li-ion intercalation. As mentioned in chapter I, during the 1970’s and 1980’s Li alloys were used as anodes in Li-batteries.\textsuperscript{12} However, the use of Li alloys in commercial cells caused a recall due to explosions.\textsuperscript{13, 14} To gain understanding of these explosions, the properties of metallic Li were analyzed and it was observed that during charging, a porous deposit was formed on the anode. This deposit caused an increase in internal pressure of the cell that led to explosions. Thus, alternate materials like graphite were suggested for use as anode. The graphitic form of carbon has the structural and functional attributes that allow reversible Li ion intercalation.\textsuperscript{15-20} This section elucidates the anode-film development process.

2.5.1 Components of an anode film

An anode film consists of the following components:

1. An anode-active material like graphite or other form of carbon.

2. Conductive additives that increase the overall conductivity of the film without undergoing any irreversible change during the charge and discharge cycles.
3. A binder material to hold the graphite and the additives together to form a cohesive film.\textsuperscript{21}

4. A solvent that can help make a slurry of all the above components to aid in spreading a layer.

5. A copper current collector that not only holds the film in place but provides the required electrical contact between the cell electrodes and the anode active material.

2.5.2 Quantitative analysis of the anode film materials

Once the components of the anode films are established, it is important to quantify them. Mixing of the above components in various proportions will produce anode pastes of different compositions and properties. It would take an era to analyze all these mixtures and determine their individual capacities. However, an understanding of the cell chemistry would help determine the ratio of the components. Since graphite is the functional unit of cell operation, it is imperative that it be present in maximum amount.

Additives are added to increase the conductivity of the anode film. Common examples of additives added to anodes are carbon black and acetylene black. Typically, the amount of additive forms 5-10\% of the total anode composition.

Composite anodes that have graphite mixed with a high capacity compounds are gaining importance. The ratios required to make an anode mixture could be determined by the desired capacity of the resultant battery. For example, the theoretical capacity of graphite is 372 mAh/g. A good example of a high capacity anode-active material is tin oxide (theoretical capacity = 791 mAh/g). Thus, in order to design a cell with 580 mAh/g
capacity, the ratio of graphite and tin oxide must be 1:1. In order to understand the calculation involved to determine the capacity of a cell, let us consider an anode ‘a’, with 1 g of total active material; 0.5 g graphite and 0.5 g tin oxide. In order to calculate the theoretical capacity of the anode ‘a’, the weights of the components is multiplied with their respective theoretical capacities. The sum of the individual capacity contribution elements is the theoretical capacity of the anode.

The binder used in the anode provides no enhancement in the cell capacity. Hence, the amount of binder material should be minimal because its role is to glue the particles of graphite or the additive or both. Too much binder might lower the cell capacity and hence is avoided. Too little binder, on the other hand, would cause the layers to be brittle, which will generate poor anode layers.

The function of the solvent is to dissolve all the components to obtain a slurry. Once the slurry is cast on the support, there is no longer a need for the solvent. Thus, a solvent should be so selected that it could be easily removed by evaporation. The support on which the film is cast should provide good adhesion characteristics with the anode active materials. In addition, it should be highly conductive to act as a current collector.

2.5.3 Properties of the anode film

Once the components and their ratios are established, it is essential to establish the characteristics of the desired anode film. Based on the discussion in the previous sections, the following characteristics of the film could be presumed:
1. The film has high capacity that could be calculated based on the theoretical capacity of graphite and its additives. If there are no additives, then all the capacity is attributed to graphite.

2. The film would adhere strongly in place on the copper current collector.

3. The graphite and the additives will form a cohesive layer.

These properties of the film are determined by its constituents and thus can be easily controlled. In addition to these characteristics, there are certain other features that define a good film. The current section is dedicated towards explanation of each of these criteria.

1. *Amount of active material*

   In addition to the ratios of each individual material, it is important to determine the total amount of material present on the support. This aspect is generally easy to calculate. High capacity Li ion batteries have active materials ranging from 10-20 mg/cm². This weight is the combined weight of graphite, additive and the binder and the capacity contribution is due to graphite and the additive only.

2. *Thickness*

   The thickness of the electrode affects the electrochemical properties of a Li ion cell. The mass transport rate of a thick electrode (say, >2 mm) is comparatively lower than a thin one. In a thick electrode, the path of mass transport is longer causing the development of a concentration gradient on the surface and the interior of the electrode during the charge/discharge cycles. Vidts et al. and Heikonen et al. have theoretically proved that the capacity of a cell decreases as the thickness of the film approaches 4 mm. Thus, thin film electrodes will have higher energy density and
specific energy levels. The energy density is defined as the energy available from the battery per unit volume of the battery. The specific energy level is the energy available from a battery per unit weight of the battery. Hence, it is desirable to have anodes of thickness less than 2 mm. This would demand that the anode film development method include a method for measuring electrode thickness or better casting electrodes of known thickness. Research shows that anode films with a thickness of 150-200 µm have produced high specific energy levels.\(^{27}\) Also, conventionally doctor blades have been used by battery manufacturers to obtain films of desired thickness.\(^{28-30}\)

3. **Porosity**\(^{31}\)

The electrode characteristics depend upon the method of preparation of electrodes. The electrochemical performance of the electrode is influenced by its porosity. Thus, it is essential to optimize the porosity of the cell. The presence of too many voids in the film would cause lowering of the capacity. On the other hand, if the active material is squeezed into a small space, there is a possibility of volumetric expansion during the intercalation charge process that could lead to explosions. Thus, the anode film porosity must be controlled along with its weight and thickness.

4. **Reproducibility**

Reproducibility of the film in terms of its weight, thickness and porosity are extremely important for efficient electrochemical analysis. Thus, the film development methods should use standardized procedures that guarantee reproducibility.
5. **Solid electrolyte interphase (SEI) and the anode**\(^{32}\)

As already mentioned, the reversibly capacity of the cell depends upon the SEI formed on its surface. If the anode film aids in formation of the SEI, the irreversible loss in capacity could be lowered. A good SEI would be a thin film with high ionic conductivity, uniformly covering the surface of the carbonaceous anode. Hence, it is crucial that the anode film is uniform to assist in formation of an even SEI film.

An anode film developmental method should be designed keeping in mind all these aspects. In the present research, the anode film development was one of the most challenging tasks. Nonetheless, anode films of known thickness were produced reproducibly. The anode film development is a complex task and could be sub-categorized into three major tasks-

1. Preparing the anode mixture for the film.
2. Spreading of layers using a mini doctor blade.
3. Calendaring to achieve desired porosity.

Before discussing each step in detail, let us get an overview of the anode film development process. The idea is to obtain anode mixture slurry consisting of the active material, the additive (optional), the binder, and the solvent. This slurry can then be spread on the copper foil using a doctor blade to control its thickness. The films obtained could then be compressed using a calendar rolling mill to optimize the porosity. The procedure seems simple but is extremely painstaking and requires careful handling of materials. The following sections discuss each step of the process in detail.
2.5.3.1 Preparing the anode mixture for the film

The graphite used was of two different types. SFG44 graphite was donated by TIMCAL Ltd (Bodio, Switzerland) due to its unavailability in the market in small quantities. SFG44 is the commonly used graphite for battery applications. It is a fine black powder with less than 0.5 % moisture content. Its specific surface area (BET) is 5 m$^2$/g with an average particle size ($d_{90}$ value) of 48.8 µm.$^{33}$ The second kind of graphite was 99.99 % pure synthetic grade graphite purchased from Alfa-Aesar.

The binder used was polyvinylidene fluoride (PVDF) and the solvent used is N-methyl pyrrolidene (NMP). Both the reagents were obtained from Aldrich Chemicals (NMP has 97 % purity). The graphite was vacuum dried at 180 °C for at least 12 h before use.$^{34}$ The anodes prepared and the electrolytes used for battery testing are non-aqueous. Hence, the vacuum oven and dry box were used to minimize the water and oxygen content. The vacuum-dried graphite was used in combination with PVDF and NMP to make thin anode films for use.$^{35}$ The current collector used was a 15 µm Furakawa copper foil donated by Mitsuya Boeki Ltd (Osaka, Japan) with the assistance of Pred Materials (New York).

The composition of anode material was an important criterion to be considered. The graphite and the binder material should be present in appropriate proportions to form stable layers with good conductivity. The general composition that is used is 90-95 % graphite and 5-10 % binder.$^{22}$ In this study, the graphite composition was always close to 90 % and that of the binder was 10 %. The anode layers compositions is as summarized in the following table:
Table 2.1  Graphite and PVDF compositions for various anodes.

<table>
<thead>
<tr>
<th>Type of Anode</th>
<th>Graphite Content (%)</th>
<th>PVDF Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFG44</td>
<td>90-92</td>
<td>8-10</td>
</tr>
<tr>
<td>Conducting Grade Gr</td>
<td>90-92</td>
<td>8-10</td>
</tr>
<tr>
<td>SnO$_2$-based Anodes</td>
<td>~45 (+ ~45 % SnO$_2$)</td>
<td>~10</td>
</tr>
<tr>
<td>Carbon encapsulated Sn-based anode</td>
<td>~80 (+ ~10 % Carbon)</td>
<td>~10</td>
</tr>
</tbody>
</table>

Typical weights of graphite were 0.4500 g and that of PVDF were 0.0500 g according to the ratios given in the table. This quantity could be spread on at least 10 (sometimes 12) anode discs with each disc weighing 10-20 mg. Copper current collector discs of 1.6 cm$^2$ area were cut using a cork hole borer, and then numbered and weighed. The weight difference of copper discs before and after transfer of material helped determine the active weight of anode and allowed theoretical capacity calculation. The anode mixture was spread on copper foils using a mini doctor blade.

Initial attempts formed uniform layers of anode mixture made using graphite, PVDF and NMP. However, these films did not adhere well to the copper disc and the film fell off as soon as the solvent evaporated. This section explains the route to solving the adhesion issues related to graphite anodes.

The first concern was the easy fragility of the anode. This was caused by improper dispersion of PVDF in graphite. Hence, various mixing methods like sonication, magnetic stirring, and hand-mixing were performed and compared. Sonicating the mixture for 5-10 min proved futile and the mixture obtained was lumpy. Magnetic stirring of the sample resulted in contamination of the sample due to the use of a magnet.
and hence was discontinued. Hand-mixing the sample using a clean stirrer was the only practicable option. The volatility and toxicity of NMP requires the use of protective gear (goggles, gloves and mask) during preparation. The volatility of NMP requires the entire procedure to be completed quickly. Hence, the PVDF was mixed with 2-3 ml NMP and stirred for 2 min and then transferred to the glass vial consisting of vacuum dried graphite powder. The mixture was then stirred vigorously for 5 min while adding few drops of NMP on the side of the vial. Once, the mixture is ready it is immediately transferred on the prearranged set up of the copper discs using the doctor blade.

For proper adhesion, the foil was pre-treated with a 2 M NaOH solution to remove surface impurities. Hand mixing of the film components and foil treatment greatly improves the anode film properties. The anode disc was dried under vacuum at 80 °C for 12-14 h. This process removed the NMP solvent from the layers and the resulting layer was extremely stable and adhered well.

2.5.3.2 Spreading of layers using a mini doctor blade

A doctor blade is an efficient tool used to produce even layers of known thickness. One such blade was designed in the lab for casting anode films of known thickness. Figure 2.10 is a photograph of the laboratory designed mini-doctor blade with the most important parts labeled. A vertical micrometer stage holds the spreader blade (a disposable safety razor blade) and is mounted on a linear travel ball-bearing stage (Edmund optics, USA). After alignment on the substrate, the micrometer allows precise control of the blade-substrate separation. The doctor blade system can be used to prepare films of about $5 \times 5$ cm. An initial zero spacing was set by positioning the blade partly
on the copper foil and verifying the absence of space and proper parallel alignment by using a paper strip to probe for gaps. If the paper did not pass through the blade and the copper foil, the screws of the vertical stage were tightened. Once calibrated, the micrometer could be set to the reading that would produce films of desired thickness.

Fig. 2.10  Schematic diagram of mini doctor blade.

The mini doctor blade is an extremely efficient instrument with simplicity of operation. Once calibrated, the anode slurry was cast on the copper foil and the linear slide was moved forward and backward in one slow motion. The blade helped spread the anode material on the disc and since the reading was set on the micrometer, the films had the appropriate thickness. The thickness of the anode films was between 150-200 µm, as determined by the micrometer positioner when the slurry was spread on the foil.
Also, since NMP is volatile, the transfer of layer on the disc and the sliding of blade needs to be quick in order to avoid solidification of the material. It is important that a fresh razor blade is used for each experiment to avoid contamination. Also, the system needs thorough cleaning before and after the experiment using distilled water and acetone. The procedure needs to be performed inside the fume hood to minimize the exposure to NMP vapors.

### 2.5.3.3 Compression of layers

The anode layers, once made using the doctor blade were transferred to a vacuum oven and dried at 80 °C for 2-3 h. Then, they were calendared using a jeweler’s calendar roller. This device is used to roll metal foils to uniform thickness and was purchased from Finding King (Mesa, Arizona).\(^{36}\) It is capable of making films as thin as 25 µm. The calendar is cleaned and set to 150 µm using feeler gauges before operation. The anode layer is then inserted between the rollers of the mill holding it carefully at one end with a pair of tweezers. The mill is rolled once and the anode is collected using the tweezers at the other end. This process is not successful on every anode layer as some times the material is lost on the rollers. However, 90% layers come out compressed to 150 µm. Also, now that there is better cohesion between the material and the current collector, surface of layer is less resistive.

Once compressed, the anode discs were transferred to the vacuum oven and dried for 12-14 h at 80 °C. The dried layers were allowed to cool under vacuum and then transferred to the glove box for testing and analysis.
In sum, this section described the detailed execution of the process of preparation of an anode film. Establishing the right system and procedures for film preparation was a challenge. However, at the end, the anode films made were reproducible in terms of thickness and strength and had an average active material of 7-15 mg/cm$^2$.

\subsection*{2.6 Cathode, Reference Electrode, Electrolyte, and Separator}

The cathode of our half cell is Li metal.$^{8,37}$ Pure Li foil, 0.03 inch thick was obtained for use as cathode from Alfa Aesar (99.9\% purity). A cork hole borer was used to cut 0.5 inch diam discs for use in cell testing.

A reference electrode is used to measure the potential difference across the cell circuit.$^{38}$ It provides an unpolarized reference potential against which the potential of working electrode can be measured. The connection between a reference electrode and the cell is established by placing the reference electrode in contact with the electrolyte solution containing a common cation or an anion. Lithium wire satisfies all these properties and hence is used as reference.$^{39,40}$ Unless otherwise noted voltages are reported versus the Li$^{0/+}$ reference (-3.045 vs. NHE).

The reference electrode used was a Li wire of 0.125 in diam. The Li wire was obtained from Alfa Aesar (99.8\% purity) in an argon filled packing. Additionally, the wire was coated with oil to prevent any reaction with air. Thus, the wire needed to be cleaned with a tissue and polished using an 800 grit sand paper before use.

The electrolyte of a Li-ion cell requires careful formulation before use. It is important to understand its function inside the cell before discussing the composition. The primary function of the electrolyte is to aid in conduction of Li-ions between the
cathode and the anode. The second very important function of the electrolyte is to form the solid electrolyte interphase (SEI). An ideal electrolyte will have high ionic conductivity and no electronic conductivity as that would lead to short-circuiting. In addition to this, the electrolyte should remain non-reactive towards electrode materials, have good temperature performance and be safe to work with. Lithium-ion batteries use a mixture of organic solvents like ethylene carbonate (EC), diethyl carbonate (DEC), and propylene carbonate (PC) and a Li-based salts like Li hexa-fluorophosphates.

The Li salt LiPF$_6$ was obtained from Strem Chemicals. The solvent mixture was composed of ethylene carbonate (99.99 % anhydrous), and diethyl carbonate (99.99 % anhydrous), both purchased from Aldrich Chemicals. The exact electrolyte composition consisted of 1:1 weight percent of both solvents.$^{41}$ Accordingly, EC and DEC were weighed on the balance inside the dry box and a stock solution was prepared. The molarity of the salt is an important criterion and after careful experimentation, 1 M solution was found to be most appropriate for use. The cell was cleaned using a propylene carbonate solvent (99.99 % anhydrous) also purchased from Aldrich.

The separator of a Li-ion battery is a microporous structure that physically separates the cathode from the anode. A glass fiber filter paper is commonly used as a separator in Li-ion batteries.$^{33,42}$ The separator material used was glass fiber filter circles of G6 type obtained from Fisher Scientific. The separator was cut into 0.5 inch discs and vacuum dried for 3 h before transferring to the dry box.
2.7 Cell Assembly

Cell construction requires the right order of placement of layers to achieve proper operation. This section first describes the arrangement inside the cell and later discusses the outer connections.

The typical arrangement inside the cell was a set of current collectors holding the anode and cathode materials in place, physically separated from each other by a separator membrane. The cell assembly was carried out inside the dry box. The cell was vacuum dried at a low temperature (~20 °C) overnight before transferring into the dry box.

The cell assembly was carried out in the following steps:

1. The anode disc was first weighed and the disc number and the weight compared to determine the weight of the active material.
2. The anode disc was placed on a glass slide. The separator was wetted with 1 M LiPF$_6$ in EC: DEC (1:1 wt%) electrolyte solution and placed on the anode disc.
3. The cell sandwich was completed by placing the Li metal disc on the filter paper.
4. The floating anode was inserted into the cavity of the body of the cell and pushed inside until it was 10 mm below the other end of the cell.
5. The Li-ion cell sandwich was then placed on the floating anode and the cathode disc was pressed straight into the cell from this end. The screws of the cathode side are tightened.
The spring was inserted into the cavity of the floating anode and the anode connector piece was pushed with a little pressure to hold the spring in place. The screws were then fastened using the hex key.

The electrolyte port was then inserted into the groove and the clamp was fastened using the screw.

The cell was then clamped horizontally on the stand with the electrolyte port facing upwards.

The port was filled with electrolyte and the reference electrode was inserted.

Thus, the cell was assembled and the horizontal cross section of the cell is represented by the Figure 2.1. The working, auxiliary and the reference electrodes are represented as they were placed in the working cell. The electrode connections represent the banana connectors present outside the cell that require external cables for establishing connection with the dry box.

2.8 Troubleshooting the cell

Initially, the cell did not perform as expected. This initiated a troubleshooting procedure to decipher the potential problems in the cell. The tests were to determine optimum working conditions for the cell and to determine if the cell leaked. The cell was tested outside the dry box for simplicity. The initial experiments produced noisy signals. Often, off-scale currents were recorded, when the amount of material could not support such high currents. A suspicion of leakage seemed to fit the observed behavior.
2.8.1 Leak Testing

The first test was to check for leaks inside the cell. The lower portion of the cell was wrapped in a Kim-Wipe and then filled with electrolyte solution. This cell was left overnight and was checked for any traces of wetness on the paper. Also, the cell was dismantled carefully and then checked for any traces of solvent. Interestingly, the portion below the fill port clamp and around the fill port was moist indicating that the area where the fill port and the body meet is the place where the leak occurs. The solution leaked from this area into the fill port clamp. When excess electrolyte was added, it overflowed onto the steel electrodes leading to an internal shorting and erroneous readings. Removal of fill port and clamp were determined to be most suitable for cell operation.

The removal of the cell port also addressed another unforeseen problem. The insertion of reference electrode into the steel fill port produced erroneous voltage readings. The voltage obtained was not against Li reference but it was the steel reference. The removal of the fill port removed this error. Leakage also occurred due to damaged O-rings. New O-rings addressed this issue.

All the above changes brought significant improvement in the voltage readings. The open circuit voltage, when compared with earlier measurements showed drastic improvements. Given below are the graphs of the cell signal before and after making the changes. The cell signal in both the cases increases continuously. However, the signal is noisy in figure one and it decreases towards the end of the cycle. This was attributed to the leaks observed in the cell. The signal in Figure 2.12 increases continuously till the end and there is little noise. Thus, it was learnt that while assembling a cell, it was very
important to ensure that all the cell components like the O-rings were in order and the electrolyte was not over filled.

![Noisy Open Circuit Voltage Signal](image1)

**Fig. 2.11** Open circuit voltage of the cell when assembled the first time.

![Good Signal](image2)

**Fig. 2.12** Open circuit voltage of the cell after making the changes.
2.8.2 Cyclic Voltammetry Testing

After the cell leak was fixed, it was important to determine if the cell was capable of testing electrode materials. Electroanalytical testing, particularly, cyclic voltammetry has been used widely for electrochemical analysis.\textsuperscript{43, 44} CV is the first study carried out during an electroanalytical study. Since the initial studies of Matheson and Nichols\textsuperscript{45} and Randels,\textsuperscript{46} CV has been utilized in various forms.

Cyclic voltammetry is the study of the working electrode using a linearly changing voltage. This potentiodynamic technique yields a cyclic voltammogram that comprises of current versus voltage curve of the electrode. The potential sweep could be set depending up on the operating limits of the cell and the potentiostat. Consider a voltage scan for a reversible redox reaction represented by the following equation:

$$R \rightleftharpoons O + ne^-$$ \hspace{1cm} (2.1)

In considering the reversibility of intercalation of the Li-ion system, cell testing using cyclic voltammetry was carried out using reversible reactions. Three different symmetrical test cells were assembled and cyclic voltammograms were obtained at scan rates of 1 mV/s. The potentiodynamic scans were carried out ±100 mV from open circuit potential (OCV) and repeated at least 5 times. The OCV of a cell is defined as the potential difference across the cell under no load conditions. At this point, theoretically no current flows into or away from the cell. The voltammograms obtained were compared with the predicted behavior to establish the functionality of the cell. Three different reference cells were assembled. Each cell and its results are discussed in the following sections.
2.8.2.1 Copper-copper symmetrical cell with copper reference

The first cell assembled was a Cu-reference cell. The working and counter electrodes were cut into 0.5 inch discs from the 15 µm copper foil obtained from Mitsuya Boeki Ltd. The reference electrode was a solid, soft drawn, bare copper wire 0.038 inch diam obtained from a local hardware store. The wire was polished with 800 grit sand paper manufactured by 3 M before use. Glass fiber filter paper was used as a separator. The electrolyte solution was 0.1 M CuSO₄ solution (Fisher scientific). The cell was assembled as per the steps discussed previously. The electrolyte solution was filled in the cavity of the plastic body and the fill port and the fill port clamp were eliminated. The open circuit potential of the cell was measured for sixty seconds.

The first voltammogram is represented in Figure 2.14. As seen in the figure, the voltammogram exhibits the behavior of the cell consisting of two non-polarizable copper electrodes. In a symmetrical system such as this, the only limitation caused to the flow of electrons is offered by the electrolyte resistance. This is clearly evident as the current peaks deviate from the ideal curve.

The open circuit potential of the system was found to be approximately 4 mV. Hence, 10 voltage ramps were carried out from -46 to 54 mV at 1 mV/s scan rate. The results obtained are displayed in the figure.
Fig. 2.13 Forward (black) and Reverse (red) voltage ramps of copper electrode cell using 0.1 M CuSO₄ solution. Scan rate is 1 mV/s.

Fig. 2.14 Cyclic voltammetry scans of the copper electrode cell.
The reproducibility of the current in each ramp suggests the stability of the cell. In addition, it suggests that the oxidation and reduction reactions occurring at the copper electrodes are completely reversible at each cycle. Additionally, this experiment shows that the total resistance offered by the cell is 160 mΩ calculated from the slope of the CV curve. This number constitutes the solution resistance between the stainless steel electrodes of the cell and behaves as a true resistance over these conditions.⁴⁷

2.8.2.2 Copper-copper symmetrical cell with silver reference

The second cell resembled the first cell in terms of its working and counter electrodes. The reference electrode used was a silver wire in 0.01 M solution of AgNO₃ (Sargent-Welch, USA). The silver wire was polished with 800 grit sand paper before use. New copper discs of 0.5 inch diam were cut using a cork hole borer.

Figure 2.16 represents the forward and reverse voltage ramp of the cell. During the forward scan, the oxidation of silver occurs and continues for certain amount of time. The cyclic voltammogram obtained displays this reversible behavior by showing identical forward and backward scans.
Fig. 2.15  Forward (black) and Reverse (red) voltage ramps of copper electrode cell using 0.01 M AgNO₃ solution. Scan rate is 1 mV/s.

The scan was repeated for ten cycles to observe the behavior of the system. The following graph shows the results. The second cycle is the only one showing irregularity and the remaining cycles are reproducible. This anomaly in the second cycle could be due to an external disturbance caused in the system. The solution resistance was comparable to the previous value.

It is important to note that the O-ring was replaced before each cell assembly to ensure proper working of the cell. Also, the amount of electrolyte was less than 1 ml and the cell was not refilled until all the experiments were completed. Also, the cell was wiped dry after filling it with the electrolyte to ensure that the electrodes and the connectors were dry always.
2.8.2.3 Graphite based cells

The previous experiments helped establish the proper working conditions of the cell. However, it was essential to conduct tests using the anode layers before placing the cell in the dry box. The idea is to be able to obtain plots and curves that could be explained with reasonable evidence. Accordingly, two cells were assembled and tested. The first cell used a SFG44 based working electrode, the one that will be used for actual half-cell testing. The auxiliary electrodes and the reference electrodes were copper. The electrolyte was a mixture of 0.1 M solution of CuSO$_4$ and 1 M LiPF$_6$ in 1:1 mixture of EC: DEC (wt %). Figure 2.18 (a) represents the cyclic voltammogram obtained for this cell.

The second cell used a similar SFG44 graphite-based anode and a copper auxiliary electrode. The reference electrode was a silver wire and the electrolyte was a
mixture of 0.01 M AgNO$_3$ solution and 1 M LiPF$_6$ in 1:1 mixture of EC: DEC (wt %).

Figure 2.17 (b) represents the cyclic voltammogram obtained for this cell.

![Graphs](image)

**Fig. 2.17** CVs of SFG44 graphite at 1 mV/s scan rate (a) Cu RE with 0.1 M CuSO$_4$/1 M LiPF$_6$ in 1:1 EC:DEC. (b) Ag RE with 0.01 M AgNO$_3$/1 M LiPF$_6$ in 1:1 EC:DEC.

Figure 2.17 (a) and (b) are interesting to analyze. In the previous experiments, the working and the counter electrodes were identical. This similarity offered identical conditions for the reactions to occur. In the current experiment, the working electrode is a carbonaceous anode and the counter is copper in both the cells. The difference in the reference electrodes and the electrolytes thus is responsible for the difference in the voltammograms. The reference electrode serves as a measure for the potential difference across the circuit and does not contribute towards cell operation. Thus, the difference in electrolyte causes the differences in voltammograms. The ionic concentration is higher in cell (a) when compared with cell (b). In cell (a), the Ag$^+$ cation is reduced to Ag metal at
carbon giving similar currents as seen with copper anode. In cell (a), the Cu$^+$ is not reduced due to kinetic limitations, and thus, the current is smaller.

To observe if the above observations were reproducible, the experiment was continued for 10 cycles. However, the 10 cycles carried out in case of these cells were different from the earlier experiment. The voltage ramp was done staring at open circuit potential after each cycle. This enabled the study of change in OCV as the reaction proceeds. This graphs obtained for two different systems were as shown in the figures. As can be seen in Figures 2.19 and 2.20, every voltage ramp is connected by a small horizontal line. This line indicates the OCV reading. The black line indicates the voltages and the red lines indicate the corresponding currents.

Fig. 2.18 CVs of the carbon electrode cell using a Cu RE. Conditions as used in Figure 2.17 (a).
The cyclic voltammograms obtained with this schedule show a different behavior. The open circuit potential changes in each successive cycle causing a change in the current in both cases. Additionally, the voltammograms are less reproducible than the previous reactions suggesting certain irreversibility in the process. However, the primary idea of these experiments was to determine the cell functionality. The results obtained were reasonable and thus the cell was considered to be ready for the actual Li-ion cell based material testing.

These experiments were followed by the actual Li-ion cell testing experiments. The cell was transferred back to dry box after cleaning thoroughly and vacuum drying the steel parts at a low temperature. The cell assembly was hereafter carried out in the dry box and the experiments on Li-ion cell materials performed.
2.9 Miscellaneous issues encountered while testing candidate materials

Once the initial troubleshooting was done and the test cell was transferred to the dry box, additional issues were found during the testing process. This section aims to acknowledge their existence and their remediation.

1. The cell performance showed inexplicable results when the dry box atmosphere was not completely pure. Regular regeneration (once per 3 mo) was used to fix this problem.

2. A cell performance might be satisfactory initially, but then decreases with time. This behavior suggested drying of the electrolyte inside the cell. Typically, the separator is dipped in the electrolyte before the cell assembly. In addition, the electrolyte port is filled up with the same solution and the experiments performed. Over the duration of the experiment, the cell might run out of electrolyte and go completely dry. Since the reference electrode is no longer in contact with the electrolyte, the measurements obtained are not acceptable. It is a good practice to refill the cell with electrolyte every 24 h when running a long experiment to ensure that the cell never goes dry.

3. As already discussed, the reference electrode is placed in the cavity and then connected with an alligator clip of the dry box electrical feedthrough. Lithium is a soft metal and the hinges of the alligator clip might break the wire when the cell is left unattended for a long time. It is always better to reconnect the reference electrode before starting a new experiment and even when refilling a cell to avoid any data corruption due to poor contact of reference electrode.
In sum, this chapter discussed the important goals that were achieved during the research. Equipping a lab with half-cell testing stage proved to be a challenging task. Nonetheless, the stage was set efficiently and the Li-ion cell electrode materials were tested. The next chapter discusses the testing schedules and the results obtained.
2.10 References


14. For example, see 'Cellular Phone Recall May Cause Setback for Moli'. *Toronto Globe and Mail* August 15, 1989.


CHAPTER III
ANALYSIS OF ANODE MATERIALS

3.1 Introduction

The anode materials of Li-ion batteries have attracted much attention during the previous years. Graphite based anode materials have been traditionally used as anodes in Li-ion batteries due to their high capacity (372 mAh/g) and lower potential (0.1-0.3 V vs. Li/Li$^+$) of its Li intercalated compound.\textsuperscript{1} The reversibility of the intercalation and the de-intercalation reaction between Li and graphite is the result of the formation of a stable solid electrolyte interphase (SEI) on the surface of the anode.\textsuperscript{2,3} The formation of SEI causes an irreversible capacity loss during the initial cycles in graphite-based electrodes. The capacity loss is affected by the electrolyte composition, the structure and chemistry of graphite surface.\textsuperscript{4,5} As discussed in Chapter I, the SEI is formed as a result of the decomposition of the electrolyte. So, the properties of SEI depend on the type of electrolyte used. Varying electrolyte composition thus varies the composition of the SEI. Extensive research has been performed on the electrolytes of Li-ion batteries and the resultant SEI formation. A mixture of organic solvents consisting of ethylene carbonate, diethyl carbonate or dimethyl carbonate with a Li-based salt has been suggested a good electrolyte for SEI formation.\textsuperscript{6-8} The structure and chemistry of graphite greatly influences the SEI formation and the present work discusses this phenomenon.
Since the Li-ion cell operates beyond the thermodynamic stability of the organic solvents used as electrolytes, the decomposition of the electrolyte occurs leading to formation of SEI. This decomposition of electrolyte consumes a fraction of Li-ion cell capacity that causes the decrease in capacity of the anode. This loss of irreversible capacity is the primary concern. It is believed that the loss can be minimized by using high capacity anodes or by surface modification of anodes. The anode capacity could be increased using additives or high-capacity anode active materials that can increase the overall capacity of the cell thus decreasing the net loss of irreversible capacity. The goal of present work is to be able to relate the SEI formation with the initial loss of irreversible capacity of the cell. The SEI formation, as discussed in chapter I, proceeds in four different stages. The staging phenomenon could be efficiently studied using the CV and charge/discharge curves. The CVs help understand the staging phenomenon and the voltage range of the intercalation. The charge/discharge curves observe the staging process in an entirely different perspective. In order to study the initial loss of irreversible capacity of anode-active material, the cycling behavior is studied. Finally, the SEM images of the anode layers before and after the experiments along with the EDS help understand the relationship between irreversible capacity loss and SEI formation.

Four kinds of anodes were tested and compared for performance. Two standard graphite materials were examined: SFG44 graphite (Timcal, Bodio, Switzerland) and conducting grade graphite powder (Alfa-Aesar, Ward Hill, MA). In addition, anode active materials used to make composite anodes like tin and tin-oxide were examined. These materials were synthesized by Beatty and Pittman group at MSU and include tin oxide spheres and carbon encapsulated tin. These materials were added to SFG44
graphite as additives in small amounts to increase the capacity and to observe the
differences in formation of SEI. This chapter focuses on the comparison of these four
different anode layers. Scanning electron micrographs were obtained for each of these
anodes before and after the experiment in order to see visible formation of SEI. Electron
diffraction study was used for elemental study of the layers.

3.2 Experimental

3.2.1 Reagents and methods

SFG44 graphite was donated by TIMCAL Ltd (Bodio, Switzerland). The current
collector used was a 15 µm Furakawa copper foil donated by Mitsuya Boeki Ltd (Osaka,
Japan) with the assistance of Pred Materials (New York). PVDF and NMP (97 %) were
purchased from Aldrich. Lithium foil (99.9 % purity) and Li wire (99.8 % purity) were
from Alfa-Aesar. Ethylene carbonate (99.99 % anhydrous) and diethyl carbonate (99.99
% anhydrous) were purchased from Aldrich Chemicals and Li-hexafluoro phosphate salt
was from Stem chemicals. Glass fiber filter circles of G6 type were obtained from Fisher
Scientific. Copper sulfate pentahydrate crystalline (blue) was from Fisher and silver
nitrate (ACS grade) was from Sargent-Welch. Titanium tetrachloride (99.9% purity) and
zinc chloride solution were from Acros Organics. Argon (compressed, UHP) was from
Airgas, Inc. The potentiostat was a Solartron 1470 E (Solartron Analytical, Hampshire,
England).
Cyclic voltammetry experiments involved two or more voltage sweeps from 0 to 2 V and back at 0.1 mV/s. A rest period of 60 s was inserted prior to each voltage cycle. The slow scan rate produces distinct peaks for the processes occurring during the ramp.

Galvanostatic charge/discharge experiments followed a simple schedule below. Between 10-50 cycles (n) were recorded at different C-rates. The following schedule is typical:

1) Rest for 60 seconds
2) Charge at \(-i\) mA until \(V_{\text{cell}} \leq 0.005\) V
3) Discharge at \(i\) mA until \(V_{\text{cell}} \geq 2\) V
4) Repeat n-1 times.

In the above schedule, ‘i’ indicates the specific current calculated based on the rate desired. Ideally, the first charge discharge cycle was a C/10 rate that was used to ensure complete SEI formation. Later, the C/5 rate was used for consecutive cycles, the number being denoted by ‘n’. Data points were every 2 mV. In addition, a reading was made at least once per minute and at a maximum of once second. The first experiment performed on each cell was two CV scans followed by a galvanostatic charge/discharge cycle. After the electrochemical measurements, the anode was removed from the cell and was observed by scanning electron microscope to determine the presence of SEI.

### 3.2.2 Results and Discussion

Li-ion battery testing yields an enormous amount of results that could be utilized to understand the technology further. During this study, two different kinds of experiments were performed. The first one was a simple cyclic voltammetry voltage
ramp between the working voltages of the cell at a very low scan rate. This scan showed distinct lithiation and de-lithiation peaks for Li. In addition, the staging phenomenon could be observed. This chapter discusses the experimental results of Li-ion cell testing in detail.

The cell was assembled as discussed in the previous chapter and the experiments were performed on it. Every aspect of a well designed experiment for analysis requires careful planning before execution. The scan rate for voltammograms could range from nV/s to V/s based on the kind of data desired. Dokko et al.\textsuperscript{12} studied the Li-insertion and extraction in single crystal LiMn\textsubscript{2}O\textsubscript{4}. They suggested that scan rates higher than 0.1 mV/s produced voltammograms with lower resolution. The peaks became indistinguishable in such voltammograms and thus could not be observed separately. At scan rate lower than 0.1 mV/s, the capacity of the electrode sustained i.e. the utilization of the LiMn\textsubscript{2}O\textsubscript{4} crystal for the electrochemical process was nearly 100 %. Lipparoni et al.\textsuperscript{13} conducted experiments to evaluate metal oxides for use as anodes in Li-ion batteries. Their cyclic voltammetry studies involved a scan rate of 0.1 mV/s.

3.2.2.1 Cyclic voltammetry of SFG44 graphite

Table 3.2 lists the details of a typical SFG44 based graphite cell that was prepared by the procedure described in chapter two. The voltage ramp was done from 0 to 2 V and back at 0.1 mV/s. The voltammogram obtained is displayed in Figure 3.1.
Table 3.1 Description of the cell used to perform the SFG44 graphite experiments.

<table>
<thead>
<tr>
<th></th>
<th>Typical SFG44 based cell</th>
<th>Cell under study</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td>90-95 % SFG44 Gr + 10-15 % PVDF + NMP</td>
<td>90 % SFG44 Gr + 10 % PVDF + NMP</td>
</tr>
<tr>
<td><strong>Active weight of anode</strong></td>
<td>1.5 to 20 mg/cm²</td>
<td>8.125 mg/cm²</td>
</tr>
<tr>
<td><strong>Auxiliary electrode</strong></td>
<td>Lithium disc</td>
<td>Lithium disc</td>
</tr>
<tr>
<td><strong>Reference electrode</strong></td>
<td>Lithium wire</td>
<td>Lithium wire</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>1 M LiPF₆ in 1:1 Wt % EC:DEC</td>
<td>1 M LiPF₆ in 1:1 Wt % EC:DEC prepared on 9/26/2007</td>
</tr>
<tr>
<td><strong>Open Circuit Voltage</strong></td>
<td>0.0047 V to 1.04 V</td>
<td>478 mV</td>
</tr>
<tr>
<td><strong>Theoretical Capacity</strong></td>
<td>0.56 to 7.4 mAh/g</td>
<td>4.836 mAh/8.125 mg</td>
</tr>
</tbody>
</table>

The graph obtained for the voltage ramp for SFG44 graphite shows the occurrence of the staging phenomenon. As can be seen in the graph, the points a, b, c, and d represent the stages IV, III, II, and I. The staging process starts at 0.9 V with stage IV. This is a quick process and is completed within a 0.1 V range. Stage III starts at 0.7 V and Stage II is complete at 0.3 V. Stage II is the longest. The intercalation process is complete by the end of stage I at 0.1 V. These results are comparable to the results obtained by Wang et al.¹⁵ discussed in Chapter one.
Fig. 3.1 Cyclic voltammogram of SFG44 graphite at 0.1 mV/s displaying four distinct peaks representative of four distinct stages of Li-ion intercalation.

3.2.2.2 Charge/discharge curve of SFG44 graphite

After two cycles, a charge/discharge experiment at a C/2 was performed. The first charge/discharge cycle is plotted in Figure 3.2.

The intercalation and the de-intercalation phenomenon occur as plateaus in the graph. The stages are not clearly visible. However, the wide plateau indicates the region of intercalation of Li into graphite. As it is known that the theoretical capacity of pure graphite (372 mAh/g) is based on composition of LiC₆ intercalated compound. The SFG44 graphite used has successfully delivered capacities as much as 50 % of the theoretical value which is impressive the given the test conditions and when compared to the studies performed by Zhang et al.¹ wherein the capacity of natural graphite was 48 % of its theoretical capacity.
3.2.2.3 Cycling characteristic of SFG44 graphite

Once the staging phenomenon was observed in the CV scans, data was collected to determine irreversible loss in capacity. The charge/discharge cycles were repeated 30 times and the data obtained was the voltage (V vs. Li/Li+) vs. time of charge or discharge. The capacity was first calculated in mAh/\(x\) mg of anode where ‘\(x\)’ is the weight of the anode. This value was then converted to mAh/g and plotted against the voltage.

The graph in Figure 3.3 shows the charge and discharge capacities for the first thirty cycles of the Li-ion cell described above. The capacity is 170 mAh/g in the initial few cycles. Additionally, during these initial cycles the charge and discharge capacities are considerably different and non reproducible. After the first 5-6 cycles, the capacity stabilizes to a particular value and remains the same for the remaining period. This
irreversible loss of capacity is attributed to the formation of SEI during the initial few cycles.

![Graph showing capacity vs cycles](image)

**Fig. 3.3** Capacity graph for first 25 cycles of SFG44 graphite-based anode showing the irreversible loss of capacity in the first 10 cycles.

The SEI formation, as discussed earlier, is an important phenomenon leading to cell stabilization. This is apparent in the graph, as the cell capacity reaches an optimum value and remains there once the SEI is formed. The SEI formation process utilizes a considerable amount of capacity of a cell and this causes the irreversibility. Also, it is important to note that the SEI formation is not complete until the end of sixth cycle in the above cell that shows that the formation of SEI is not limited to first couple of cycles but may proceed further.

The theoretical capacity of SFG44 graphite of 372 mAh/g is definitely achievable. However, as previously mentioned, the results obtained in the present project are...
comparable to the literature data obtained by few groups. For example, the initial
capacity of graphite obtained by Zhang et al.\textsuperscript{1} was 48 \% and the capacity achievable in
our experiments was 50 \%. This result is encouraging as both the capacities are obtained
under identical test conditions.

The data obtained for the intercalation and de-intercalation phenomena in the
present experiments is interpreted based on the observations made by other groups. The
results show that the behavior of graphite is identical in both cases. Nonetheless, the
major area of concern in the present experiments is low capacity of graphite than
theoretical. It has been suggested by Zhang et al.,\textsuperscript{1} that improving techniques related to
anode layer development would improve the capacity. Ball milling graphite mixture
before making the anode layer has been widely used and documented to deliver excellent
capacities.\textsuperscript{16}

Various cells were constructed for experiments. However, only a few cells
showed the anticipated behavior of SFG44 graphite. A majority of the cells did not last
beyond the CV scans and thus had to be dismantled. However, the data presented in the
current work is of the cells that worked beyond the initial CV scans. The following table
(3.2) lists the average capacities of the cells that seemed to show the typical SFG44
graphite behavior.
As is evident from the table, the difference in capacities in the cell is large. The working of the cell depends on various factors ranging from the method of anode layer development to the final cell assembly. It is difficult to pinpoint the reason for the inability of the cell to perform. Nonetheless, the data presented here serve as a good representative of a good working cell of SFG44 based graphite. Also, it should be noted that the same is applicable to all the cells discussed in this chapter.

### 3.2.2.4 SEM analysis of SEI on SFG44 graphite

In order to corroborate the presence of SEI, scanning electron micrographs of the cell anode were obtained. A technique known as electron diffraction spectrum (EDS) has been successfully employed for elemental analysis in combination with SEM imaging. The EDS study was used to determine the composition of the SEI formed. This study not only aided in confirming the presence of SEI layer, but also helped in identifying the
components present in it. To promote comparative qualitative analysis, micrographs of an uncharged, freshly prepared anode were obtained first. These pictures provided a basis to understand the structure and distribution of graphite on copper. The second set of images was of the anode layer that has been dipped in electrolyte. These pictures could be used for a comparative analysis with the third set that consisted of the anode that has been subjected to at least two CV scans at 0.1 mV/s and thus has the SEI film. Additionally, the elements present on each set of images were confirmed using the EDS study. The following section discusses the SFG44 graphite micrographs and the corresponding EDS spectrum.

SFG44 graphite revealed various important structural characteristics when its SEM images were analyzed. The first two images represent the SEM micrographs of a SFG44 graphite anode obtained at 500 X and 1000 X magnification respectively. The flaky structure of graphite is clearly visible in the image. Additionally, the average flake size of 44 µm is apparent in the image. The ball-like structures are the PVDF binder that hold the sample together.
Fig. 3.4  (a) SEM image of a SFG44 graphite-based anode at 500 X resolution before testing. (b) SEM image of a SFG44 graphite-based anode at 1000 X resolution before testing.

Fig. 3.5  EDS spectrum of SFG44 graphite-based electrode showing evidence for carbon. The image shows the point of interest for which the spectrum is obtained.
Fig. 3.6 EDS spectrum of SFG44 graphite-based electrode showing evidence for PVDF. The image shows the point of interest for which the spectrum is obtained.

Figure 3.5 and 3.6 represent the point of interest to obtain an EDS spectrum. The histogram clearly shows the peaks for carbon and oxygen indicating their presence. The elemental atomic weight percentages of carbon and oxygen were found to be 98.49 % and 1.51 % respectively. These numbers indicate graphite. It is important to note that the graphite was vacuum dried before analysis. However, exposure to atmosphere during transportation of the sample for analysis resulted in oxygen contamination, which is displayed as a peak in the spectrum.

The white-colored clusters show the presence of carbon and oxygen along with fluorine. The weight percentages of carbon and fluorine were 75.57 % and 23.78 % respectively. These values suggest that the clusters are PVDF particles. As already explained, the tiny oxygen peak is representative of oxygen contamination.

The electrolyte used in Li-ion batteries is capable of precipitation and thus causing damage to the electrode. It is therefore essential to be able to distinguish between electrolytes that might have precipitated on the surface from SEI layer. Thus, this image
serves as a reference to distinguish between SEI films from any kind of precipitation. In addition to this, it has already been discussed that the decomposition of the electrolyte during the operation of a battery causes the formation of SEI. Thus, the composition of SEI would be similar to the composition of the electrolyte used. The above histogram helps confirm the elements of the electrolyte and thus could be used for comparative analysis for the SEI images.

To prepare a sample for the second set of images, a fresh SFG44 graphite-based anode was completely wet with electrolyte solution. A small bottle of electrolyte was removed from the dry box and poured on to the anode layer using a dropper. The layer was then dried in the fume hood for at least 16-18 h. Before performing SEM analysis, it was observed under the optical microscope to ensure it had no traces of electrolyte.

The next two images are the micrographs at 500 X and 1000 X magnification of the anode sample that has been prepared using the above procedure. The most striking difference between these images and the previous anode images is the disappearance of PVDF particles. The addition of electrolyte has caused dissolution of the PVDF and thus it is no longer visible. The EDS spectrum of these images yields data that could help confirm the presence of electrolyte on carbon.
Fig. 3.7  (a) SEM image of SFG44 graphite-based electrode dipped in electrolyte at 500 X resolution before testing. (b) SEM image of SFG44 graphite-based electrode dipped in electrolyte at 1000 X resolution before testing.

Fig. 3.8  SEM micrograph of SFG44 anode dipped in electrolyte showing peaks for the components of electrolyte.

Figure 3.8 shows the presence of carbon, oxygen, fluorine and phosphorous. The peaks for carbon, oxygen and fluorine are higher than that of phosphorous indicating a greater amount of these substances. The electrolyte solution consists of EC: DEC and LiPF$_6$ salt. Also, the atomic percentages of carbon, oxygen, fluorine and phosphorous are
91.30 %, 6.28 %, 0.70 % and 1.73 % respectively suggest the presence of traces of electrolyte on carbon flakes.

Figure 3.9 (a) and (b) show the SEI film on SFG44 graphite-based anode that has been subjected to two slow CV scans to complete the formation of SEI and are obtained at 500 X and 1000 X respectively. The graphite flakes appear to be covered with a film that may represent the SEI. As can be seen in the images, the putative SEI film is thick and covers at least 90 % of the anode when formed. Also, it is interesting to note the change in shape of the flakes of graphite. In earlier images, the edges of the shape were sharp and more geometrically defined. After the formation of SEI, the edges of the graphite appear to be more curved. As seen earlier, the PVDF is no longer distinguishable and has been dissolved by the electrolyte. The components of the SEI were confirmed by an EDS spectrum, the graph of which is displayed below.
The EDS study reveals the presence of carbon, oxygen, fluorine and phosphorus in the following weight percentages – 31.70, 21.81, 38.00 and 8.50 respectively. This data thus confirms that the film is a decomposition product of the electrolyte and is thus a SEI film. Additionally, the elemental composition of carbon, oxygen and fluorine has increased considerably when compared to the earlier anodes. These data thus help establish the presence of SEI on the carbon anode.

The characteristics of the SEI film formed on SFG44 graphite are comparable to the literature data. This film is not as thick as the VC-derived films seen in the results of Shim et al.\textsuperscript{17} The film formation is considerably fast based on the explanation of Buqa et al.\textsuperscript{14} that could be attributed to the particle size of graphite. A comparative picture of SEI formation on other anodes will help appreciate the present observations.

The interactions between anode, cathode, and the electrolyte result in the formation of SEI. The SEI is composed of various materials like LiF, LiCO\textsubscript{3}, LiCO-R, Li\textsubscript{2}O, Li alkoxides, and more.\textsuperscript{18,19} Unfortunately, Li cannot be detected using EDS. However, the occurrence of other elements suggests that these salts might be present. As
evident from the capacity graph, an optimized SEI could be formed in the initial few cycles of charge/discharge. Once the formation is complete, the capacity loss is much smaller and is due to the impedance of carbon anodes.\textsuperscript{20,21,22}

Thus, SFG44 graphite has a good reversible capacity and the loss of capacity during the first few cycles could be associated with the formation of the SEI. These experiments and observations serve as a reference point to compare the performances of conducting grade graphite and the tin-oxide based electrodes.

3.2.2.5 Cyclic voltammetry of conducting grade graphite

The conducting grade graphite obtained from Alfa-Aesar is a recommended battery anode material by the manufacturer. The conducting grade graphite has a granularity distribution of -325 mesh size.\textsuperscript{23} The conducting grade graphite yields results that are very different from those obtained at SFG44. The CV scans and the charge/discharge experiments were performed on the cell described in table 3.3.
Table 3.3  Cell description of the conducting grade graphite-based Li-ion cell.

<table>
<thead>
<tr>
<th></th>
<th>Typical cell</th>
<th>Values for the cell under study</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td>90-95% conducting grade Gr + 10-15% PVDF + NMP</td>
<td>90% conducting grade Gr + 10% PVDF + NMP</td>
</tr>
<tr>
<td><strong>Active weight of anode</strong></td>
<td>1.5 to 30 mg/cm²</td>
<td>27.1 mg</td>
</tr>
<tr>
<td><strong>Auxiliary electrode</strong></td>
<td>Lithium disc</td>
<td>Lithium disc</td>
</tr>
<tr>
<td><strong>Reference electrode</strong></td>
<td>Lithium wire</td>
<td>Lithium wire</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>1 M LiPF₆ in 1:1 Wt % EC:DEC</td>
<td>1 M LiPF₆ in 1:1 Wt % EC:DEC prepared on 11/16/2007</td>
</tr>
<tr>
<td><strong>Open Circuit Voltage of the cell</strong></td>
<td>0.0047 V to 2 V</td>
<td>1.98 V</td>
</tr>
<tr>
<td><strong>Theoretical Capacity</strong></td>
<td>0.56 to 11.16 mAh/g</td>
<td>10 mAh/27.1 mg</td>
</tr>
</tbody>
</table>

The graph obtained for the voltage ramp is displayed below in Figure 3.11. The graph displays peaks spread between 0.6 to 0.09 V. A closer examination of these peaks reveals the stages of Li-ion intercalation into graphite. Stage IV begins at around 0.6 V indicated by a small peak. This peak is not sharp but decays gradually until the stage is complete which is at about 0.42 V. Stages III and II are represented by a wide peak between 0.32 to 0.2 V. Finally, the LiC₆ is formed and the intercalation is said to be complete at stage I. The intercalation is said to be complete at around 0.05 V.
The cyclic voltammogram of conducting grade graphite does not display peaks as defined as in case of SFG44 graphite. Since the test conditions and solutions are identical, the difference could be attributed to the difference in the graphite used. The conducting grade graphite particles are larger than the SFG44 graphite particles (Figure 3.4 and 3.14). As already discussed in chapter I, Buqa et al.\textsuperscript{14} suggested the affect of the particle size on the performance characteristics of the anode. According to them, graphite with larger particle size has lower capacity. The cyclic voltammogram is used to study the peaks for the first intercalation and reveals no significant differences between both SFG44 and conducting grade. Nonetheless, the charge/discharge data and the cycling information will certainly help establish notable differences between the two.

![Cyclic voltammogram of conducting grade graphite-based Li-ion cell obtained at 0.1 mV/s scan rate showing the stages of Li-ion intercalation with carbon.](image)

**Fig. 3.11** Cyclic voltammogram of conducting grade graphite-based Li-ion cell obtained at 0.1 mV/s scan rate showing the stages of Li-ion intercalation with carbon.
It is important to understand that the Li-ion intercalation is characteristic of the kind of graphite used. Although, the voltage range for each stage of intercalation might overlap, the individual stages would occur at the specific intercalation voltage of a particular kind of graphite. The differences in intercalation voltages of SFG44 graphite and conducting grade graphite offer more credibility to this observation.

3.2.2.6 Charge/discharge curve of conducting grade graphite

The conducting grade graphite-based cell was subjected to a cyclic voltammetric scan for two cycles. This was followed by the galvanostatic charge discharge of the cell at C/5 rate. The charge/discharge curve of the conducting grade graphite was analyzed to observe the staging phenomenon. Figure 3.12 displays one of the initial galvanostatic charge/discharge curves obtained for conducting grade graphite using the same cell described above. In order to be able to obtain distinct stages of intercalation, a slower scan rate of C/5 was used to obtain the curve. Unfortunately, this slow rate was not capable of producing distinct plateaus for each stage.
As can be seen in the graph, the plateaus to represent the staging phenomenon are not distinct. However, the stages can be correlated with the voltages observed in the cyclic voltammogram. In addition to the staging phenomenon, it is interesting to observe that the above cell is capable of delivering 100 percent of its charge capacity as the charge and discharge curves are almost identical. This denotes that the cell is capable of exhibiting good amount of reversibility.

### 3.2.2.7 Cycling characteristic of conducting grade graphite

The C/5 rate galvanostatic experiments were continued for 10 cycles. As can be seen in the graph below, the data obtained shows a small decrease in capacity. This is attributed to the formation of SEI. However, there is no significant change in capacity and hence it comes back to the initial after the 10th cycle. This demonstrates that the
conducting grade graphite is characterized by a very small loss in irreversible capacity.

The anode did not undergo charge or discharge experiment after the first 10 cycles indicating very low cycle life. The observation could be explained based on the SEM images obtained that are discussed later.

![Fig. 3.13 Capacity graph for the first 10 cycles of conducting grade based Li-ion cell showing the insignificant irreversible loss of capacity of the anode.](image)

Each set of experiments with a particular kind of anode active material required the construction of at least five cells of which only a couple worked as expected. The following table lists the three cells that showed anticipated behavior for conducting grade graphite. As can be seen in the table, the capacity delivered by all the working cells is closely related. In addition, these cells did not cycle well and this was attributed to the quality of SEI formed on the surface.
Table 3.4 Table listing the details of various working cells that were assembled for conducting grade graphite-based anode with their average capacities.

<table>
<thead>
<tr>
<th>Cell Number</th>
<th>Date of cell Assembly</th>
<th>Average capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5th November 2007</td>
<td>72.4</td>
</tr>
<tr>
<td>2</td>
<td>11\textsuperscript{th} November 2007</td>
<td>89.6</td>
</tr>
<tr>
<td>3</td>
<td>22\textsuperscript{nd} November 2007</td>
<td>68.5</td>
</tr>
</tbody>
</table>

The difference in results obtained in SFG44 graphite and conducting grade graphite could be interpreted based on the observations made by Ning et al.\textsuperscript{24} According to them, the larger particle size of graphite in conducting grade graphite (~325 mesh) causes it to accumulate more Li. This, along with high current density causes a faster SEI formation. However, the SEI formed is non-uniform, defective (has cracks) and thick. Thus, the irreversible capacity loss is minimal. A good SEI formation, as seen in case of SFG44 graphite (average particle size of 44 µm) consumes more capacity than observed in this case. These results are confirmed by the SEM analysis of conducting grade graphite discussed in the next section.

3.2.2.8 SEM analysis of SEI on conducting grade graphite

The presence of SEI in the anodes based on conducting grade graphite was confirmed by performing SEM analysis. The first set of images, shown below represents the nascent anode that has not been subjected to any experimental analysis. The first image is obtained at 500 X resolution and it shows the amorphous flakes of conducting grade graphite with PVDF particles holding them together. The graphite flakes vary
greatly in their size and distribution. The second image is obtained at 1000 X resolution and it shows the variation in size of graphite flakes in greater detail. EDS analysis was performed to confirm the elements.

Fig. 3.14  (a) SEM micrograph showing the anode layer of conducting grade graphite at 500 X resolution before testing. (b) SEM micrograph showing the anode layer of conducting grade graphite at 1000 X resolution before testing.

The EDS analysis shown in the following figure displays the spectrum obtained for graphite flake. The carbon and oxygen have weight percentages of 97.42 and 2.48 % respectively. These reading confirm that the flaky area in the image represents graphite and the small amount of oxygen has only been adsorbed on the surface during transfer from the vacuum oven to the SEM analyzer.
Fig. 3.15 EDS spectrum of conducting grade graphite-based anode showing the evidence for carbon. The image shows the exact point for which the spectrum is obtained.

The next point of interest was to confirm the presence of PVDF. As shown in the spectrum below, the carbon, oxygen, and fluorine are present in 79.2 %, 1.47 % and 19.33 %. It is interesting to note that the PVDF is not evenly distributed in conducting grade graphite. In SFG44 graphite, the distribution of PVDF was more uniform. The procedure involved in preparation of both kinds of anodes is similar and hence, the difference observed could be attributed to the kind of graphite used. It was observed that the anode layers prepared from conducting grade graphite were extremely fragile and fell apart very easily. The SEM analysis helped establish that the weak layers might result from the unevenly distributed PVDF. Thus, it was learnt that additional stirring was necessary while preparing these electrodes to promote PVDF distribution.
Fig. 3.16 EDS spectrum of conducting grade graphite-based electrode showing the point of interest in the image. The peaks suggest the presence of PVDF.

The next set of images shown below is of the anode layers dipped in the electrolyte. The two images are obtained at 500 X and 1000 X resolutions respectively. The images show traces of electrolyte on carbon and the PVDF no longer is distinguishable. The spectrum following the images is the EDS of a point of interest on a 1000 X image of the anode. The four named peaks of carbon, oxygen, fluorine, and phosphorous have the weight percents of 54.1, 10.69, 30.08, and 5.12% respectively. In addition to this, another tiny anonymous peak is observed in the spectrum that has been identified as copper. The presence of copper indicates that the point of analysis has a very thin coating of the active material and hence the X-rays were able to detect copper.

The presence of sum peaks has been a consistent problem with EDS analysis. A sum peak is the result of the addition of the peak values of previously identified elements. The elements capable of producing a sum peak in the following graph are carbon, oxygen, and fluorine. A sum peak for carbon and oxygen would occur at 0.8 keV and that for carbon and fluorine would occur at 1.0 keV. The oxygen and fluorine would produce
a sum peak at 1.2 keV. However, this peak occurs at 0.915 keV that does not coincide with these values. Thus the possibility of a sum peak is ruled out. The elemental analysis suggests the peak might represent copper and this suggestion is acceptable as the electrodes are cast on copper foil.

Fig. 3.17 (a) SEM micrograph of the conducting grade graphite-based anode dipped in electrolyte at 500 X resolution before testing. (b) SEM micrograph of the conducting grade graphite-based anode dipped in electrolyte at 1000 X resolution before testing.

Fig. 3.18 EDS spectrum of conducting grade graphite-based electrode representing the components of the electrolyte.
Fig. 3.19 (a) SEM micrograph of conducting grade graphite-based cell anode showing the SEI at 500 X after testing. (b) SEM micrograph of conducting grade graphite-based cell anode showing the SEI at 1000 X after testing.

The images shown in Figure 3.19 represent the SEI film on the electrode at 500 X and 1000 X respectively. The anodes show dense clouds of SEI at certain places while the other areas remain uncovered. This suggests that the SEI formation is incomplete which might be a possibility as these cells were subjected to two CV scans before analysis. As discussed earlier, the formation of SEI requires at least a few initial cycles and this fact is confirmed by the above micrograph. The presence of SEI is confirmed by taking an EDS spectrum that shows the presence of carbon, oxygen, fluorine, and phosphorous. The point of interest on the micrograph and its corresponding spectrum are displayed below.
Fig. 3.20 EDS spectrum of conducting grade graphite-based anode layer showing the peaks for SEI components.

The EDS spectrum shows four sharp peaks for carbon, oxygen, fluorine and phosphorous in weight percentages of 12.68, 7.55, 22.55, and 57.22 % respectively. The ratio suggests the presence of phosphorus and fluorine based salts of Li. The SEI is responsible for optimizing the performance of the cell after causing an initial irreversible loss. The conducting grade graphite-based cells deliver only a fraction of their theoretical capacity. This could be explained based on the observations made in the micrographs. The anode layers made from conducting based graphite are highly brittle due to poor dispersion of PVDF. This kind of layer might have lower ability to hold Li than its corresponding SFG44 based layer. Thus, the loss in irreversible capacity due to SEI formation combined with the inability of the graphite to hold greater amounts of Li accounts for the lower capacity of conducting grade graphite. Nonetheless, this layer has an equal charge and discharge capacity that makes it a good candidate for consideration for Li-ion battery anodes.
3.3 Comparison of Sn-based anode material to traditional materials

Commercial Li-ion batteries use graphite intercalation compounds (GICs) as anode active materials. The capacity offered by these compounds is limited to 372 mAh/g and hence composite anode materials with higher capacities are desired. Of the newer materials, tin-oxide composites were suggested as attractive materials for Li-ion batteries. The theoretical capacity of Sn is 791 mAh/g, which is almost double of what carbon offers. Dahn’s and Chen’s research groups studied the mechanism of Li ion intercalation into tin oxide and proposed a two step process. In the presence of Li, the SnO\textsubscript{2} undergoes reduction leading to the formation of Li\textsubscript{2}O. This is an irreversible reaction and causes a large decrease in the irreversible capacity of the electrode. The reaction can be represented as follows:

\[ \text{SnO}_2 + 4\text{Li} + 4e^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O} \]  \hspace{1cm} \text{(3.1)}

Sn formation occurs between 1 and 1.2 V. The peak for tin reduction occurs at 1.2 V. The next reaction involves reversible intercalation of Li into the tin to form the Li\textsubscript{x}Sn complex as described in the following equation:

\[ \text{Sn} + x\text{Li} + xe^- \rightleftharpoons \text{Li}_x\text{Sn} \hspace{0.5cm} (0 \leq x \leq 4.4) \]  \hspace{1cm} \text{(3.2)}

The peak for the above reaction occurs at around 0.25 V. Tin oxide based electrodes are becoming popular due to their high capacity and the low potential of Li-ion intercalation.

Winter et al. conducted studies on the tin-based Li alloying materials and collected some important information. Lithium-alloy formation occurs at ~1.0 to ~0.3 V vs. Li/Li\textsuperscript{+} while the intercalation of Li into graphite occurs at ~0.2 to ~0.1 V. This
property of Li alloy causes the cell to have lower cell voltages consequently decreasing the energy density and specific energy. The large gap between the potentials of Li-alloy formation and the Li deposition reduces the safety problems that occur during rapid charge due to Li deposition on the host material. Another important characteristic of metal based electrodes is that they do not undergo solvent co-intercalation. On the other hand, these metals suffer from major structural and volume changes during alloy formation that discourages their use in Li-ion batteries. The Li-Sn alloy could be represented by the formula Li^{x+}Sn^{x-}. While forming this compound, the host material incorporates positive Li ions and the corresponding negative charges. The charge transfer reaction resulting in the formation of Sn^{x-} is represented below:

\[ \text{Sn}^0 + x \text{e}^- \rightarrow \text{Sn}^{x-} \quad (3.3) \]

The resultant Sn^{x-} anions are considerably less dense than neutral Sn\(^0\) atoms. As a consequence of alloying, the lithiated host is 100-300 % larger in volume. In addition to this large expansion, the Li alloys have considerably high ionic character that causes them to be extremely brittle.\(^{36}\) The mechanical stress experienced due to volumetric expansion lowers the mechanical stability of the anode thus causing pulverization. Pulverization refers to the cracking or crumbling of the electrode resulting in loss of electronic inter particle contact.\(^{37}\) Thus, unless properly designed a metal based electrode fails after first few charge/discharge cycles.
3.3.1 Cyclic voltammetry of SnO$_2$-composite anode

The preparation of composite electrode of SnO$_2$ and SFG44 graphite were based on the parameters listed in the table 3.5. The capacity of the cell was calculated based on the relative capacities of the components. In our study, the cell had equal amounts of SnO$_2$ spheres and SFG44 graphite by weight and thus, the capacity contribution from each component was equal.

Table 3.5   Cell description of a SnO$_2$-SFG44 graphite-based cell.

<table>
<thead>
<tr>
<th></th>
<th>Typical range</th>
<th>Cell under study</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td>10-80 % SnO$_2$ + 80-10 % SFG44 Gr + 10 % PVDF + NMP</td>
<td>45 % SnO$_2$ + 45% SFG44 Gr + 10 % PVDF + NMP</td>
</tr>
<tr>
<td><strong>Active weight of anode</strong></td>
<td>1.5 to 20 mg/cm$^2$</td>
<td>20.56 mg/cm$^2$</td>
</tr>
<tr>
<td><strong>Auxiliary electrode</strong></td>
<td>Lithium disc</td>
<td>Lithium disc</td>
</tr>
<tr>
<td><strong>Reference electrode</strong></td>
<td>Lithium wire</td>
<td>Lithium wire</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>1 M LiPF$_6$ in 1:1 Wt % EC:DEC</td>
<td>1 M LiPF$_6$ in 1:1 Wt % EC:DEC prepared on 11/16/2007</td>
</tr>
<tr>
<td><strong>Open Circuit Voltage of the cell</strong></td>
<td>1.0-2.0 V</td>
<td>1.2 V</td>
</tr>
<tr>
<td><strong>Theoretical Capacity</strong></td>
<td>372 mAh/g for SFG44 graphite and 791 mAh/g from SnO$_2$ spheres</td>
<td>5.35 mAh/18.5 mg</td>
</tr>
</tbody>
</table>
The first set of experiments performed was a CV scan from 0 to 2 V and back at scan rate of 0.1 mV/s. The cyclic voltammogram appears as shown in the graph below. Since the anode is composed of tin oxide and graphite, there are two types of intercalations that occur. The first kind involves graphite and the intercalation occurs in four distinct stages. The second reaction is the allowing of tin and Li in two steps. In the graph, the peak labeled ‘c’ is composed of two sharp peaks. Since, two intercalation reactions occur simultaneously, there is a good possibility of peak overlap of Li$_x$C and Li$_x$Sn. Thus, it is assumed that the additional peak at 0.18 V most probably represents the intercalation reaction between Li and tin.

The four stages of graphite-Li intercalation have been labeled as a, b, c, and d. The four distinct peaks occur at 0.61, 0.3, 0.21, and 0.04 V represent stages IV, III, II, and I respectively.

Fig. 3.21 Cyclic voltammogram of SnO$_2$-SFG44 graphite-based electrode representing the reduction of tin and the peaks for intercalation of Li into tin and carbon.
As seen from the voltammogram, the data is in good agreement with the literature data. Xue et al.\textsuperscript{38} conducted experiments using a tin-oxide based thin film electrode. Their experiments were based on the earlier experiments conducted by Mohamedi et al.\textsuperscript{39} The anodes were SnO\textsubscript{2} films prepared by laser deposition method. The first three cyclic voltammetry scans obtained by Mohamedi et al. are displayed in Figure 3.22. The scan rate used was 0.2 mV/s. As can be seen in the graph, the second and third cycles are considerably different than the first one.

Fig. 3.22 Cyclic voltammogram of tin-oxide thin film electrode for the first, second and third cycles. Figure reprinted from reference \cite{39}.
The peak labeled ‘A’ in Figure 3.22 represents the irreversible peak for tin reduction. Thus, it is absent in the second and the third cycles. The alloying of tin into Li is a reversible process that is responsible for the capacity value of 791 mAh/g. This reversible peaks are visible in all the three cycles and are labeled b and c. The cyclic voltammetry curves of SnO₂-based composite anode materials are discussed in the next section. This suggests that the cell works properly. The irreversible capacity loss and the SEI formation were observed in the next set of experiments.

3.3.2 Charge/discharge curve of SnO₂-composite anode

The voltage ramp was followed by a galvanostatic charge/discharge experiment at C/2 rate for 75 cycles. The first charge/discharge curve is plotted in Figure 3.23.

![Charge/discharge curve of SnO₂-SFG44 graphite-based electrode showing the reduction plateau for tin and intercalation plateaus for the staging phenomenon.](image-url)
The charge/discharge curve plotted above shows a very low capacity. The theoretical capacity of a composite SnO$_2$-graphite-based electrode is the sum capacity offered by each of the components. SnO$_2$ has shown theoretical capacities of 791 mAh/g and pure graphite has a 372 mAh/g capacity. Thus, the overall capacity of a SnO$_2$-SFG44 graphite-based electrodes is 580 mAh/g. Unfortunately, the capacity demonstrated by the anode layers has been extremely disappointing. The possible reasons for this low capacity could be explained based on the SEM images and this will be discussed a little later. The purpose of the graph above is to display the intercalation voltage range of Li. However, the peak for reduction of SnO$_2$ is distinctly noticeable. Another important observation that can be made in the graph is the reversibility of the anode layer. The working electrode shows equal charge and discharge capacities and this makes the electrode more desirable for further studies.

### 3.3.3 Cycling characteristic of SnO$_2$-composite anode

The charge/discharge experiments were continued for 75 cycles and the results are plotted in the graph below. As seen in the graph, the capacity drops quickly during the initial cycles. This huge loss in irreversible capacity is a characteristic feature of SnO$_2$ based electrodes and has been the major area of concern because it causes a sharp decrease in the capacity of the electrode. After the first 25 cycles, the capacity continues to fade slowly. The charge and discharge capacities in the graph are similar in value and this attributes the electrode with good reversibility.
The significant capacity fade observed in the SnO$_2$-SFG44 graphite composite electrodes was related in part to the SEI formation and to the volumetric expansion of tin. As discussed previously, the huge loss in irreversible capacity is due to the mechanical stress introduced into the anode during the alloying and de-alloying of Li from tin. The loss during initial cycles is greater because the shrinkage and expansion of tin during the initial cycles is larger than in the subsequent cycles.

Various cells were assembled to understand the cycling behavior of SnO$_2$-SFG44 graphite based anode. The following table lists the data for the cell showing cycling behavior close to the anticipated one. As can be seen in the table, the capacity difference between cell 1 and the cell 2 and 3 is huge. The capacity of cell 1 is almost double that of cell 2 or 3. The possible explanation for the difference in capacity could be based on
difference in reproducibility of anode development process. However, the results with capacities of cell 1 would definitely be more intriguing than the cell 2 or 3.

Table 3.6  Table listing the details of various working cells that were assembled for SnO$_2$-SFG44 graphite-based anode with their average capacities.

<table>
<thead>
<tr>
<th>Cell Number</th>
<th>Date of cell Assembly</th>
<th>Average capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9$^{th}$ December 2007</td>
<td>186.22</td>
</tr>
<tr>
<td>2</td>
<td>14$^{th}$ December 2007</td>
<td>74.5</td>
</tr>
<tr>
<td>3</td>
<td>28$^{th}$ December 2007</td>
<td>77.5</td>
</tr>
</tbody>
</table>

Xue et al.$^{38}$ performed charge/discharge experiments on Sn-based electrodes for 50 cycles. The initial discharge capacity was 1426.2 mAh/g and that for the second cycle was 1179.8 mAh/g. The tin based electrode retained only 82 % of its original capacity in one cycle. The subsequent cycles show a further decrease in the capacity. The lowest capacity observed was 564.6 mAh/g. This continual loss in irreversible capacity was attributed to volumetric expansion of tin that causes pulverization of the anode. Furthermore, it is assumed that if the experiment is continued further, the capacity would drop to zero.

Winter et al. obtained SEM data for the SEI formation on tin-based electrodes.$^{43}$ The degradation of host electrode is clearly evident in the images. The formation of SEI is the major factor that causes the irreversible capacity loss in graphite-based electrodes. In tin-oxide composite electrodes, the SEI formation is accompanied by the volumetric expansion of the electrode that consumes certain capacity. The volumetric expansion
caused on alloying of Li during the first cycle is the maximum. The subsequent expansion and shrinkage are smaller. The SEM images were taken for the anode layers before and after the experiments to see the change in morphology of the electrode.

3.3.4 SEM analysis of SnO$_2$-composite anode

The SEM micrographs of SnO$_2$-SFG44 graphite-based composite anodes were obtained. The data obtained gave a good understanding of the morphology of the electrodes and thus helped understand the process.

![SEM micrographs](image)

Fig. 3.25 (a) SEM micrograph of SnO$_2$-SFG44 graphite-based electrode at 500 X resolution before testing. (b) SEM micrograph of SnO$_2$-SFG44 graphite-based electrode at 1000 X resolution before testing.

The first set of images shown above represents the anode layer of a composite SFG44-SnO$_2$ based electrode. The images show three distinct features representing the three components – SFG44 graphite flakes, SnO$_2$ spheres and PVDF binder. The SnO$_2$ spheres are perfectly smooth and well defined and hence are easily distinguishable from
the bushy PVDF orbs. The amorphous SFG44 graphite flakes appear to fill the rest of the image. It is important to know that both SnO$_2$ and SFG44 graphite are present at a 1:1 weight percent. However, the heavy metal tin appears to be in a lesser amount than graphite. The presence of all the three components was confirmed by EDS spectra that are shown in Figure 3.26.

![EDS spectrum of SnO$_2$-SFG44 graphite showing the point of interest and histogram showing the evidence for graphite.]

The first spectrum is obtained to corroborate the presence of graphite. As seen in the spectrum, the two peaks of carbon and oxygen have a weight percent of 97.22 and 2.78 % respectively. The trace amounts of oxygen represent contamination from atmosphere. The second spectrum shown below is obtained for PVDF. The weight percents of carbon, oxygen, and fluorine are 76.43, 1.60, and 21.97 %. The occurrence of this huge amount of fluorine thus confirms the presence of the compound.
Fig. 3.27 EDS spectrum of SnO$_2$-SFG44 graphite showing the point of interest and histogram showing the evidence for PVDF.

Fig. 3.28 EDS spectrum of SnO$_2$-SFG44 graphite showing the point of interest and histogram showing the evidence for tin.

The additional spectrum for SnO$_2$ is obtained for this SnO$_2$-SFG44 graphite-based anode. The spectrum clearly shows a large amount of tin and oxygen to demonstrate the presence of the compound. The weight percents of the compounds carbon, oxygen and tin are 1.29, 29.37, and 69.33 % respectively. This data thus confirmed the presence of all the elements in the anode layer. Thus, the next set of images were obtained for the anode layer dipped in electrolyte and are discussed below.
The SnO$_2$-SFG44 graphite-based anode was dipped in 1M LiPF$_6$ in 1:1 wt % of EC: DEC solution. The anode was air dried for 36 h and then analyzed using SEM. The images were obtained at 500 X and 1000 X resolution and are shown in Figure 3.29.

![Fig. 3.29](image)

(a) SEM micrograph of SnO$_2$-SFG44 graphite composite electrode dipped in electrolyte at 500 X before testing. (b) SEM micrograph of SnO$_2$-SFG44 graphite composite electrode dipped in electrolyte at 1000 X before testing.

The presence of electrolyte dissolves the PVDF and thus, it is no longer visible. However, a closer look at the image reveals the tin oxide spheres coated with a layer of electrolyte. Thus, it is possible that the addition of electrolyte does not cause dissolution of the SnO$_2$ powder. The EDS spectrum was obtained for the above graph and the observations were not very different from the observations made in the previous graphs. The spectrum, as shown below, shows peaks for carbon, oxygen, fluorine and copper. The weight percents of these compounds are 19.86, 4.19, 51.54 and 24.42 % respectively.
The data that correlates to the observation and the presence of electrolyte is thus confirmed.

Fig. 3.30  EDS spectrum of SnO$_2$-SFG44 based composite electrode showing the components of electrolyte on the electrode.

In addition to these peaks, an additional anonymous peak occurs at 1.45 keV. As discussed earlier, the data from the previous peaks might add up to produce a sum peak in the spectrum resulting in an erroneous peak. This most certainly is the data pertaining to the sum peak of carbon, oxygen and fluorine which occur at 0.3, 0.5 and 0.7 keV and thus producing a small error sum peak at 1.4 keV which could be ignored for further analysis.
The SnO$_2$-SFG44 graphite-based electrode was tested using cell-test and then observed under the SEM. The images shown above show the SEI at 500 X and 1000 X resolution. Before discussing the images, it is important to understand the characteristics of SnO$_2$ based electrodes.

The formation of Sn from SnO$_2$ is an irreversible reaction that leads to formation of Li$_2$O. This reaction leads to a considerable loss of capacity during the initial cycles. In addition to this, the loss is also due to the formation of SEI. In carbon-based electrodes, the capacity fade is minimized after the formation of SEI. Unfortunately, the capacity continues to decrease in tin-based electrodes. This is explained based on volume expansion experienced by the tin spheres on repeated charging and discharging. The volume change is as much as 300 % and this could induce additional electrolyte decomposition even after the SEI is formed thus increasing the loss of capacity. Thus, in
additional cycles, the Li$_2$O formation and the electrolyte decomposition continues and the capacity decreases consistently.

In addition to the above explanation for capacity loss, the SEM images show a rather thick SEI when compared to the films on carbon-based electrodes. The formation of a thick SEI would cause a greater decrease in the loss of irreversible capacity and thus would add up to lowering the performance of the cell.

An EDS spectrum was obtained to confirm the SEI layer seen in the images. The data obtained is shown in the histogram below. The SEI layer consists of carbon, oxygen, fluorine and phosphorus, the components resulting from the decomposition of electrolyte. In addition, various peaks for tin are observed indicating its presence. A weight percent measure shows 2.06, 21.05, 6.10, 3.93 and 66.86 % of carbon, oxygen, fluorine, phosphorous, and tin. The high percentage of tin in the layer suggests the occurrence of irreversible reactions and volume expansions.

Fig. 3.32 EDS spectrum of SnO$_2$-SFG44 based anode showing the components of SEI.
Thus, the low capacity of SnO$_2$-SFG44 graphite-based electrodes could be explained based on the SEM images. SnO$_2$ has the potential for being a promising anode for Li-ion batteries. However, the problems related to volume expansion and poor cycling ability need to be addressed before it could be satisfactorily used in battery applications.

3.4 Comparison of carbon encapsulated Sn-based anode material to traditional materials and to SnO$_2$ spheres

The use of tin as anode material for Li ion batteries offers a very promising capacity. Nonetheless, the problems posed by the metal compounds discourage their use. As discussed earlier, certain modifications made to tin might reduce the problems of volumetric expansion and thus offer a high capacity anode material. Various alternatives of tin based compounds has been suggested in the form of SnO$_2$ nanorods,\textsuperscript{42} polycrystalline SnO$_2$ nanotubes,\textsuperscript{43} SnO$_2$ nanowires,\textsuperscript{44} carbon supported SnO$_2$ nanoparticles and carbon-SnO$_2$ duplex nanotubes.\textsuperscript{45} The operation procedure would be a two step process wherein the reduction of oxide occurs to form tin followed by formation of Li-tin alloys. The tubular tin and tin in carbon form seems the most promising solution to overcome the volumetric expansion problem of tin.

Graphite can be prepared as carbon nanotubes (CNTs) and can be used as an anode for Li-ion batteries. The CNT morphology offers higher surface area and electrical conductivity. In addition to this, the intercalation could occur inside the nanotubes and in between them improving the overall capacity of the anode. However, CNT suffer from low volumetric capacity due to the presence of internal void that has nothing to do with Li storage and a specific capacity limited by the theoretical capacity of graphite of 372
mAh/g. Thus, the capacity of the CNT could be increased by filling in the interior of the tube with a high capacity Li-storage compound like tin, antimony or silicon. A carefully designed chemistry for this CNT encapsulated metal would thus produce a compound with high capacity and cyclability. The use of tin with carbon as an anode is discussed in the present section.

The carbon encapsulated tin was obtained from Mr. Sang Ho Lee, who prepared these by using a procedure called ‘chemical vapor deposition (CVD)’. The ethylene flow rate was 20 sccm and the temperature used was 750 °C. The morphology of the compound is interesting as it consists of a nano rod of tin enclosed in a carbon capsule. The tin nano rod has a diameter of ~80-150 nm and the surrounding carbon capsule is approximately 100-180 nm. The following figure shows the schematic diagram of a tin nanorod enclosed inside a carbon capsule. The diameter of the nano rod and the surrounding carbon are displayed.

![Schematic diagram of a carbon encapsulated tin. Figure redrawn from reference [48].](image)

As discussed earlier, though tin has an impressive capacity of alloying with Li, its use as an anode in Li-ion batteries is still restricted due to its volumetric expansion. Using
a nanoscale tin material may help to reduce the pulverization. Additionally, the surrounding graphite would discourage greater expansion of tin thus preventing huge expansions and the consequent breakdown of the material. Thus, the carbon encapsulated tin is considered to be a more promising alternative to the regular tin based materials.

3.4.1 Cyclic voltammetry of carbon encapsulated Sn-SFG44 graphite-based electrodes

The anode layers prepared had a 3:1 ratio by weight of SFG44 graphite and carbon encapsulated tin. These two materials comprised 90% of the total weight of the anode and the remaining 10% was the binder PVDF. All the components were mixed in presence of NMP and cast on 15 µm copper foil using a doctor blade. These layers were dried for a couple of hours and then calendared using a calendar mill to 135 µm thick layers. After calendaring, the layers were dried at 80 °C under vacuum for at least 12 h. The layers obtained so were transferred to the dry box where in they were tested using a Li counter and reference electrodes. The electrolyte used was 1 M solution of LiPF₆ in 1:1 Wt % EC: DEC. The details of the cell are summarized below:
Table 3.7  Table explaining the details of a typical cell versus the cell under present study.

<table>
<thead>
<tr>
<th></th>
<th>Typical cell</th>
<th>Cell under study</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td>$x:y$ ratio of SFG44 gr: Carbon encapsulated Sn where $x$ and $y$ could be based on the desired capacity</td>
<td>3:1 ratio SFG44 Gr: Carbon encapsulated Tin + PVDF + NMP</td>
</tr>
<tr>
<td><strong>Auxiliary Electrode</strong></td>
<td>Li disc</td>
<td>Li disc</td>
</tr>
<tr>
<td><strong>Reference Electrode</strong></td>
<td>Li wire</td>
<td>Li wire</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>1 M LiPF$_6$ in 1:1 wt % EC: DEC</td>
<td>1 M LiPF$_6$ in 1:1 wt % EC: DEC prepared on 01/15/2008</td>
</tr>
<tr>
<td><strong>Active material weight</strong></td>
<td>1.5 – 20 mg/cm$^2$</td>
<td>18.4 mg/cm$^2$</td>
</tr>
<tr>
<td><strong>Theoretical Capacity</strong></td>
<td>Based on the weight ratio of the composite</td>
<td>3.95 mAh/16.6 mg</td>
</tr>
</tbody>
</table>

The first experiment performed was a slow potentiodynamic voltage scan ranging from 0 to 2 V and back. The scan rate used was 0.1 mV/s and this slow scan ensures that the peaks for intercalation and de-intercalation are distinctly visible.
Fig. 3.34 Cyclic voltammogram showing the four distinct stages of Li-ion intercalation with carbon encapsulated tin.

As can be seen in the above voltammogram, the four distinct peaks are marked as a, b, c, and d. These four peaks occur at 0.9, 0.75, 0.62 and 0.2 V represent the stages IV, III, II, and I respectively. In addition to the Li intercalation to graphite, there is the alloying of tin compound and Li. The last peak at 0.2 V is the highest. This is the combined peak representing the final stage of Li ion intercalation into graphite and the alloying of Li and tin.

The graph obtained is in good agreement with the literature data as all the stages can be distinctly observed. Guo et al.\textsuperscript{49} prepared multi-walled carbon nanotube (MWNT)-Sn composite and tested it with respect to bare MWNT and bare Sn electrodes. The cyclic voltammetry curves obtained by them are displayed in Figure 3.35. As seen in the figure, a pair of oxidation and reduction peaks occurs at 0.02 and 0.1 V corresponding to lithiation and de-lithiation of MWNT and MWNT-Sn nanocomposite. Four anodic peaks
are seen at 0.5, 0.62, 0.71 and 0.79 V that correspond to Li extraction in Sn in MWNT-Sn nanocomposite electrode. The cathodic scan shows only two corresponding peaks. In addition to this, an irreversible peak is seen above 1.0 V that represents the electrolyte decomposition. This suggests that the irreversible capacity loss during the first cycle is minimal.

![Cyclic voltammograms of MWNT-Sn composite electrode for the first, second and third cycles. Figure reprinted from reference [49].](image)

Fig. 3.35 Cyclic voltammograms of MWNT-Sn composite electrode for the first, second and third cycles. Figure reprinted from reference [49].

It is important to note that the peak for reduction of SnO₂ is no longer visible. This is obvious because the metal Sn is enclosed inside the nanotube and not the oxide.

The CV scan was followed by charge/discharge experiments discussed in the next section.
3.4.2 Charge/discharge of carbon encapsulated Sn-SFG44 graphite-based electrodes

![Charge/discharge curve](image)

Fig. 3.36 Charge/discharge curve of carbon encapsulated tin-SFG44 composite anode showing the four distinct stages of Li-ion intercalation.

The cyclic voltammetry experiments were followed by a C/5 rate charge/discharge experiment for 25 cycles. The first galvanostatic curve is displayed in Figure 3.36. The peaks that were clearly visible in the cyclic voltammogram are no longer visible during the charge discharge experiment. The theoretical capacity delivered by the compound is less than 50%. However, the charge and discharge cycles are completely reversible. As discussed in the literature review of SFG44 graphite, the engineering conditions of the electrode are responsible for the lower efficiency. The reversibility of the electrode was further examined by plotting the charge/discharge capacity as a function of cycle number.
3.4.3 Cycling characteristic of carbon encapsulated Sn-SFG44 graphite-based electrodes

The cell was charged and discharged repeatedly for 25 cycles at C/5 rate (1.5 mA). The above graph represents the first charge/discharge cycle at this rate. As can be seen in the graph, the electrode exhibits 100 % reversibility. This good cycling characteristic could be attributed to the morphology of the carbon encapsulated tin. To further corroborate this observation, the charge and discharge capacities were plotted for the 25 cycles that the experiment was run. The following figure represents the capacity graph for the electrode.

Fig. 3.37 Graph showing the charge and discharge capacities for the first 25 cycles of carbon encapsulated tin SFG44 composite anode.

As can be seen in the graph, the charge capacity is equal to the discharge capacity during each cycle. There is a decrease in capacity during the initial 10 cycles. However, after this initial loss, the capacity stabilizes and remains the same for the next consecutive cycles. This capacity loss could be attributed to the formation of solid electrolyte interphase (SEI). This result again is in good agreement with the results of Guo et al.49
The focus of the research done by Guo et al. was to compare the properties of carbon encapsulated Sn compounds with bare CNT and bare Sn. The charge/discharge cycles were continued for up to 20 cycles and the results analyzed. The nanocrystalline CNT-Sn show higher capacity when compared to CNT or bare Sn. Additionally, the capacity loss per cycle in CNT-Sn based electrode is only 0.99%. After 20 cycles, the capacity retention of these electrodes is 65% which shows their efficiency. Unlike the conventional tin-based electrodes that suffer from large volume increase, the integrity of CNT-Sn electrodes is preserved due to the small size of the composite. The nano-size tin particles undergo very little expansion on alloying with Li. Moreover, the ductility of CNT surrounding tin is easily absorbed. As a result, the volume change in CNT-Sn is negligibly small.

The data suggests that the volumetric expansion of tin is no longer taking place and most amount of the irreversible capacity loss is due to the SEI formation. In addition to this, the SEI analysis is important especially in this case to see if tin is present. The absence of tin in SEI would suggest two things: First, the complete irreversible capacity loss is attributed to SEI formation. Second, Sn plays negligible role in the formation of SEI. Thus, the SEM images were obtained for these electrodes to confirm these points. Unfortunately, due to time constraints, it was not possible to perform repeated cycling experiments for carbon encapsulated tin based anode. The reproducibility in behavior is thus the area that needs further research. The next section discusses the SEM data obtained for the SFG44-carbon encapsulated tin based electrodes.
3.4.4 SEM analysis of carbon encapsulated Sn-SFG44 graphite-based electrodes

Following the trend, three sets of SEM images were obtained. Two were the before and after experiment anode pictures and the third one was a picture of the anode layer dipped in electrolyte. Figure 3.38 (a) and (b) shows the CNT encapsulated Sn-SFG44 graphite-based anode before experiment at 500 X and 1000 X resolution. The graphite flakes with interspersed PVDF particles is clearly visible. The areas encircled in both these images show a cluster of carbon encapsulated tin and are blown up in the image 3.38 (c). At 50,000 X resolution, the carbon encapsulated tin is individually observed. The brighter outline indicates the carbon sheath and the denser part inside indicate the tin metal. EDS study was performed to corroborate the results and is displayed in the subsequent images.
Fig. 3.38 SEM micrograph of the carbon encapsulated Sn-SFG44 composite anode showing the bare anode before testing. (a) at 500 X resolution (b) at 1000 X resolution (c) at 50,000 X resolution showing the individual carbon tubes encapsulating tin.

Figure 3.39 shows the EDS spectrum for the graphite flakes. As seen in the spectrum, the only peaks visible are for carbon and oxygen. As previously discussed, the oxygen contamination occurred during the transport of the sample for analysis. The weight percents of carbon and oxygen are 97.42 % and 2.58 %. 
Fig. 3.39 EDS spectrum of carbon encapsulated Sn-SFG44 graphite-based electrode showing evidence for SFG44 graphite. The image shows the exact point of interest for which the spectrum is obtained.

Figure 3.40 shows the EDS spectrum for identification of PVDF particles. The three peaks visible on the spectrum are for carbon, fluorine and oxygen in weight percentages of 75.91, 1.12 and 22.97% respectively.

Fig. 3.40 EDS spectrum of carbon encapsulated Sn-SFG44 graphite-based electrode for PVDF. The image shows the exact point of interest for which the spectrum is obtained.
The third spectrum, shown in Figure 3.41 was obtained for the carbon encapsulated tin. As seen in the spectrum, four peaks are visible. The carbon, oxygen and tin peaks are in the weight percentages of 46.97, 0.88, and 50.53 %. The peak labeled nitrogen occurs in at weight percent of 1.62 %. Since there is only one peak present before the nitrogen peak, the possibility of this peak being an erroneous sum peak is ruled out. However, the elemental analysis on the program revealed that the occurrence of the peak at 0.438 keV could either be a peak for tin or for nitrogen. Since tin is the compound that is present for sure, it is thus confirmed that the peak represents tin and not nitrogen.

Fig. 3.41 EDS spectrum of carbon encapsulated Sn-SFG44 graphite-based electrode showing evidence for carbon. The image shows the exact point of interest for which the spectrum is obtained.

The next set of images represents the micrographs obtained for anodes dipped in 1 M solution of LiPF$_6$ in 1:1 Wt % EC: DEC electrolyte. Figure 3.42 (a) and (b) are the images obtained at 500 X and 1000 X resolution. The graphite flakes are covered in electrolyte and the PVDF particles are no longer visible. This suggests that the electrolyte dissolved the PVDF. However, there are small orb-like structures clearly visible at the
surface. These structures are the carbon enclosed Sn particles and should not be confused with PVDF. An EDS analysis was performed to confirm the observations and the results are displayed in Figures 3.43 and 3.44.

![SEM micrograph of the carbon encapsulated Sn-SFG44 composite anode showing the anode dipped in electrolyte at 500 X resolution before testing.](image1.png)

![SEM micrograph of the carbon encapsulated Sn-SFG44 composite anode showing the anode dipped in electrolyte at 1000 X resolution before testing.](image2.png)

**Fig. 3.42** (a) SEM micrograph of the carbon encapsulated Sn-SFG44 composite anode showing the anode dipped in electrolyte at 500 X resolution before testing. (b) SEM micrograph of the carbon encapsulated Sn-SFG44 composite anode showing the anode dipped in electrolyte at 1000 X resolution before testing.

Figure 3.43 is the spectrum to show the presence of electrolyte covering the anode active materials. Consequently, it displays four distinct peaks, one each for carbon, oxygen, fluorine and phosphorous. The electrolyte is composed of carbon, fluorine and phosphorus. The presence of oxygen indicates exposure of the electrode to air. The weight percentage of carbon, oxygen, fluorine, and phosphorous is 93.41, 2.53, 3.71 and 0.34 % respectively.
Fig. 3.43  EDS spectrum of carbon encapsulated Sn-SFG44 graphite-based electrode showing evidence for electrolyte. The image shows the exact point of interest for which the spectrum is obtained.

Fig. 3.44  EDS spectrum of carbon encapsulated Sn-SFG44 graphite-based electrode showing evidence for carbon. The image shows the exact point of interest for which the spectrum is obtained.

The spherical structures in the micrographs were assumed to be the carbon encapsulated tin. To corroborate this observation, EDS study was performed and the results are displayed in Figure 3.44. As seen in the spectrum, the peaks occur for carbon, oxygen, fluorine and phosphorous. In addition to these elements, peaks occur for tin, thus
showing that these spherical structures are carbon encapsulated tin covered by the electrolyte.

As discussed previously, the objective of obtaining the images of anode dipped in electrolyte is to be able to distinguish between the SEI and precipitation of electrolyte on the surface of the anode. Thus, the next set of images was of the electrode that was subjected to electrochemical analysis. The images are displayed in Figure 3.45 (a) and (b) and their corresponding EDS spectrum in Figure 3.46.

![Fig. 3.45](image)

(a) SEM micrograph of the carbon encapsulated Sn-SFG44 composite anode showing SEI at 500 X resolution after testing. (b) SEM micrograph of the carbon encapsulated Sn-SFG44 composite anode showing SEI at 1000 X resolution after testing.

Figure 3.45 (a) and (b) are obtained at 500 X and 1000 X respectively. The image at 500 X resolution closely represents the image observed by Ng et al.\(^{50}\) The SEI is a thick film in this case when compared to the bare SFG44 graphite electrodes. However, the thickness is lesser when compared with the SEI of SnO\(_2\)-composite electrode. This
might indicate the absence of tin in this film. EDS analysis is displayed in Figure 3.46 and as per our observation, there is no trace of tin.

![Fig. 3.46 EDS spectrum of carbon encapsulated Sn-SFG44 graphite-based electrode showing evidence for SEI. The image shows the exact point of interest for which the spectrum is obtained.](image)

The quantitative analysis of the carbon, oxygen, fluorine and phosphorous peaks indicate a weight percentage of 12.65, 15.80, 63.72, and 7.83 % respectively. The EDS analysis was done at different points to thoroughly establish the absence of tin. Thus, the observations made during the study of the cycling behavior of carbon encapsulated Sn-based composite anodes was established. Thus, the absence of tin shows that the irreversible capacity loss observed in these electrodes is due to SEI formation only. Additionally, tin has no direct role in formation of SEI and thus is absent in the EDS study.

Thus a comprehensive analysis of four different materials for use as anodes in Li ion batteries were tested and evaluated. The SFG44 graphite is the most common electrode material employed by battery manufacturers to make high-capacity batteries.
The conducting grade graphite has been suggested to be a good candidate for battery experiments. The SnO$_2$-graphite-based composites are the latest trends in the Li-ion battery research. The carbon encapsulated Sn represent a new era of tin based anode composites. The comparison of capacities and cycling ability of each of the graphite under similar conditions show the highest values for SFG44 graphite. Thus, it could be concluded that SFG44 graphite is the most promising material to be used in Li-ion batteries until all the issues related to the more recent materials are thoroughly addressed.
3.5 References


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CHAPTER IV

CONCLUSION

Lithium-based battery research is no more than four decades old. Nonetheless, the huge amount of research going on around the world creates an illusion of the battery research in this area being older. The initial set up of a lab to build and test batteries is a challenging process. The stage to build a battery anode involves various instruments and techniques that require time and practice. The lab now has all the equipment to be able to simulate the conditions of a manufacturing facility to make anodes. The doctor blade can adjust thickness to a very accurate value and the calendar roller could compress the electrodes efficiently.

The cell utilized for testing the materials has been successfully corrected for defects. The dry box has the right set of conditions for testing the home made Li-ion cell. The dry box has been equipped with various ports to be able to carry out testing for three different cells which we hope to do in future. Also, the Solartron potentiostat serves as a brilliant instrument to perform cell testing experiments. The software used (cell Test) allows many complicated experiments could be designed and run aiding an efficient cell analysis.

Once the testing stage was successfully set, the battery testing experiments yielded satisfactory results. Four different anode materials were tested-SFG44 graphite,
conducting grade graphite, SnO$_2$-based composite anode, and carbon encapsulated tin-based composite anode. The SFG44 graphite was thoroughly analyzed. This graphite was utilized to set the charging limit for the Li-ion battery test materials as 5 mV. This graphite was cycled for up to 150 cycles at various C-rates and the ideal C/2 to C/5 rate was determined to be most optimal. Thus, once the standard was established, the experiments were carried out on different anode active materials and the results discussed.

The idea was to compare the already existing materials with the newer ones to establish credibility. As expected, the SFG44 graphite yielded most promising results and it can be said without doubt that it is currently the most desirable material for battery industry. The conducting grade graphite is considered to be as efficient as SFG44 graphite for use in Li-ion batteries. The results obtained prove otherwise. The conducting grade graphite is harder to cast into layers and this deficiency leads to poor performance. An additional factor that might be responsible for the unexpected behavior is the method used to develop the anode film. A standard procedure discussed in Chapter 2 has been universally applied to make the anode materials. Since, the morphology of conducting grade graphite is rather different than that of the SFG44 graphite; it might require a different approach to make anode discs. This could bring about a significant change in the cycling characteristics and is an important area for research.

Tin oxide based compounds are being explored to be considered as battery anode materials. The high theoretical capacity offering of SnO$_2$-based composites has triggered the battery engineers’ interest in the compound. However, the various problems that the SnO$_2$ suffers with are yet to be addressed. The volume expansion and continued
electrolyte decomposition cause an unwanted capacity fade phenomenon. Thus, SnO$_2$-based electrodes are still at an initial stage of consideration. The volume expansion problems have been dealt with decreasing the size of tin. The expansion of a nano-sized tin material would be proportionate to the expansion of a macro-sized one. This expansion in the nano-sized material thus will be significantly lesser and could potentially address the volume expansion problem of tin. A nanocomposite of tin in the form of carbon encapsulated tin offers a promising future for the use of tin in battery anodes. The carbon encapsulated Sn produced a very little irreversible capacity loss and had good cycling efficiency. Nonetheless, the carbon encapsulated tin must be tested for performance under more stringent conditions to be able to corroborate its desirability. Based on all the test results, the SFG44 graphite has been rightly chosen to build batteries for today’s requirement.

The future Li-ion battery anode materials could definitely be tin-based. The nanosized tin particles enclosed in a carbonaceous sheath offer a good cycling capacity as discussed in the results. A thorough testing of this material at various C-rates ranging from 5C to C/20 is required to understand their cycling characteristics. This area should form the focus of future researchers.