Investigations on anode materials for rechargeable lithium-ion batteries

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INVESTIGATIONS ON ANODE MATERIALS FOR RECHARGEABLE LITHIUM-ION BATTERIES

A thesis submitted in fulfillment of the requirements for the award of the degree

Honours Master of Engineering

from

University of Wollongong

by

Jia Zhao Wang, B. Sc.

DEPARTMENT OF MATERIALS ENGINEERING

1999
ACKNOWLEDGEMENT

I would firstly like to express my deep gratitude to my supervisors, Professor H. K. Liu and Professor S. X. Dou for their academic guidance, financial support and constant encouragement throughout the project. I wish to express my sincere thanks to the co-supervisor Professor Doug Bradhurst for his great assistance during the thesis writing and helpful comments on the manuscript of thesis.

Many thanks should go to Mr. G. X. Wang, Mr. J. Chen, Mr. L. Sun, Ms. C. Y. Wang, Mr. R. Zheng, Mr J. McKinnon, Mr. X. L. Wang, Mr. X. K. Fu, Mr. C. Rossi, Dr. V. Rouessac, Dr. P. Yao, Dr. M. Ionescu and all the members at the Institute for Superconducting & Electronic Materials, and to all the technicians at the Department of Materials Engineering. Thanks are also go to Mrs. B.M. Allen, Mrs. R. Cambareri and Mrs. J. De Mestre for their help in official matters.

I wish to express my deep respect to my parents and mother-in-law and gratitude to my sister and brother for their encouragement and endless love during my studies.

Finally, I wish to extend my deepest gratitude to my husband Shi Zhong and my daughter Ershuo Zhong for their love, understanding and patience, especially to my husband who helped and encouraged me greatly throughout my studies.
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Abstract

The aim of this study is to investigate the anode materials for lithium-ion rechargeable batteries. Major interests are in the syntheses, the electrochemical characterisation and the pre-lithiation treatment of these anode materials. Three different systems of materials were synthesised and investigated in this study, they were tin-based materials, carbon-based materials and a conductive ceramic compound.

Tin oxide composite materials have been reported recently as new anode materials for rechargeable lithium-ion cells. This is due to their higher specific capacity and higher volumetric energy density compared to the graphite or carbon anode which is currently used in commercially available rechargeable lithium-ion batteries. In this study, tin oxide composites, $Sn_{1.0}B_{0.56}P_{0.40}Al_{0.42}O_{3.6}$, $Li_2SnO_3$, $SiSnO_3$ and $SnO_2$ were synthesised. The electrochemical properties of these tin oxide composites as anodes for rechargeable lithium-ion battery were investigated by using XRD analysis, CV, EIS and cyclic test through a test cell. A sol-gel method was also used to prepare the $SnO_2$ powder. Because much fine particles and homogeneous particle size distribution can be obtained by the sol-gel method, the capacity of $SnO_2$ electrodes prepared by the sol-gel method was much higher than that of $SnO_2$ without the sol-gel treatment. It was identified if the voltage cut-offs were selected appropriately the capacity retention can be improved. Better cycling performance was obtained at a voltage range between 0.3V and 1.0V for the $SnO_2$ anode. Among those tin-based anodes, the capacity of $SnO_2$ (over 400mAh/g) is the highest. Tin oxide composites represent a new class of material for the anode of Li-ion batteries, however, further research is required before tin-based oxides can be applied to commercial Li-ion batteries.
Carbon-based materials are considered as the most promising anode materials for rechargeable Li-ion batteries because of their high cycleability, good volume stability and safety. In this study, three carbonaceous materials were synthesised. Five types of carbonaceous materials - glassy carbon, polyurethane carbon, sugar carbon, graphite, and carbon black, were tested as the anodes. Among those carbon-based materials, graphite shows the highest discharge capacity and the lowest reversible capacity, while the glass carbon (GC) shows poor capacity, but the best cycling behavior. The effect of pyrolysis temperature on the carbon anode was investigated on the sugar carbon only. Results shown that the capacities of sugar carbon increased as the pyrolysis temperature ($T_p$) increased. A pre-lithiation treatment was also applied to the sugar carbon. After the treatment, the surface morphology of the samples was modified. SEM examinations on the electrode surface shown that the particle sizes were reduced and became more uniform. The reversible capacity was reduced but not significantly and not as expected. It is thought that further improvement could achieve by optimising the pre-lithiation process. To detail identify the pre-lithiation mechanism, however, further experiments are required, but it is beyond of this study.

A conductive ceramic, barium metaplumbate ($\text{BaPbO}_3$), was also synthesised and investigated as a possible anode for the rechargeable Li-ion battery. Results from this study shown that lithium ions could be electrochemically intercalated in and de-intercalated from $\text{BaPbO}_3$. These intercalation and de-intercalation reactions occur at the voltage range from 0 to 0.7 V versus Li/Li$^+$. The results shown that only pure phase $\text{BaPbO}_3$ provided a good cycleability, while a two phase compound, $\text{BaPbO}_3(\text{PbO})_x$, presented a poor cycleability. The gravimetric capacity of the $\text{BaPbO}_3$ is in the order of
110 mAh/g and a volume capacity of 960 mAh/cm³. Since this material has high inherent electronic conductivity and a good cycle behaviour, it could be used as an anode without any conductive additives. However, non-pure phase BaPbO₃ oxides, such as BaPbO₃(PbO)ₓ compound could have a different reaction mechanism. To identify the mechanism, further study is also needed.
1.1 Introduction to Secondary Lithium Batteries

1.1.1 Historical Development of Secondary Lithium Batteries

Lithium is a very attractive as a battery anode material because of its light weight, high voltage, high electrochemical equivalence, and good conductivity. Research into lithium batteries began in the 1950s when it was noticed that Li-metal was stable in a number of nonaqueous electrolytes [1]. This stability was attributed to the formation of a passivation layer that prevents the direct chemical reaction between lithium metal and the electrolyte but still allows lithium to go into solution during cell discharge. The commercialisation of lithium primary batteries followed relatively quickly in the late 1960s and 1970s. However, the development of rechargeable lithium batteries was much slower. Cycling of the metallic lithium anode in organic electrolytes showed that this anode was not completely reversible. Lithium was lost during each cycle. Metal deposited during charging could only be partially stripped during discharge due to corrosion and passivation [2]. Beginning in the early 1970s, one approach to solve this problem was to go to molten salt systems (LiCl-KCl eutectics) using a Li-Al alloy anode [3] and a FeS cathode. Room temperature rechargeable system development received a new push when Exxon was announced its intentions to commercialise the system Li/TiS$_2$ in the mid 1970s as a coin cell for electronic watches [4]. Since then, large numbers of rechargeable systems with different cathode materials, lithium metal or
different lithium compound based anodes and electrolytes have been investigated and developed. Table 1.1 shows an overview of the sequence of development of components and system for rechargeable lithium batteries.

Table 1.1 Overview of the sequence of development of components and system for rechargeable lithium batteries [5]

<table>
<thead>
<tr>
<th>Year</th>
<th>Development of components</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>anode</td>
<td>cathode</td>
</tr>
<tr>
<td></td>
<td>lithium metal (Li)</td>
<td>transition metal sulfides</td>
</tr>
<tr>
<td>1970s</td>
<td>lithium alloys</td>
<td>(TiS(_2), MoS(_2))</td>
</tr>
<tr>
<td></td>
<td>transition metal oxides</td>
<td>solid inorganic electrolytes</td>
</tr>
<tr>
<td></td>
<td>selenides</td>
<td>polymer electrolytes</td>
</tr>
<tr>
<td></td>
<td>discharged cathodes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(LiCoO(_2), LiNiO(_2))</td>
<td></td>
</tr>
<tr>
<td>1980s</td>
<td>Li-intercalation</td>
<td>manganese oxide</td>
</tr>
<tr>
<td></td>
<td>(LiWO(_2))</td>
<td>(Li(_x)MnO(_2))</td>
</tr>
<tr>
<td></td>
<td>Li-carbon (LiC(_{12}))</td>
<td>manganese spinels</td>
</tr>
<tr>
<td></td>
<td>(coke)</td>
<td>(LiMn(_2)O(_3))</td>
</tr>
<tr>
<td>1990s</td>
<td>Li-carbon (LiC(_6))</td>
<td>manganese spinels</td>
</tr>
<tr>
<td></td>
<td>(graphite)</td>
<td>(LiMn(_2)O(_3))</td>
</tr>
</tbody>
</table>

\(^a\) LE stands for liquid organic electrolyte; \(^b\) PE for polymer electrolyte
Up to the end of the 1980s, the main focus was on the systems with lithium metal anode and transition metal chalkogenide cathodes. Initial promises of very high energy densities made in the 1970s had to be reduced when it was discovered that a fairly large amount of excess lithium metal was required to achieve more than a few cycles of the anode.

On the cathode side, many of the intercalation compounds had either a fairly low voltage (e.g. 1.8 V for Li_xMoS_2 vs Li/Li^+) or were not reversible over a wide concentration range, x. The highest values for energy density reported today are over 150 Wh/kg and 300 Wh/l for laboratory cells which is after all considerably higher than any other electrically rechargeable room temperature system.

However, despite great effort the safety problem of the metallic lithium anode in liquid organic electrolytes could not be solved. In 1989, the first system that had been used commercially in consumer application, Li/MoS_2 had to be withdrawn from the market because of venting with fire in the hands of users. These events have reduced the expectations that the metallic lithium/organic liquid electrolyte system will ever be suitable for consumer applications.

At about the same time, the lithium-ion (Li-ion) technology had become attractive due to the use of lithium-carbon intercalation anodes. In 1990, the first product based on C/LiCoO_2 was announced. Excellent cycle life and a higher level of intrinsic safety were demonstrated.

What makes the Li-ion concept even more attractive is the possibility to use a low cost manganese oxide cathode which was demonstrated in 1992. Furthermore, this makes the lithium battery system also a contender for the electric vehicle battery and other large battery application [6].
1.1.2 Significance of Lithium-Ion Batteries

It is well known that Li-ion batteries have many advantages over traditional rechargeable batteries. These advantages include: high output voltage, high energy density, free from pollution. In addition, they have an energy storage efficiency and charge/discharge efficiency which comparatively greater than those of other rechargeable batteries [7].

Higher Voltage

Portable electronic equipment has typical operating voltages between 3-12V. For some equipment such as cellular telephones which have operating voltages above 3V, there is a trend to lower the operating voltage to 3V. A battery based on Ni/Cd or Ni/MH chemistry requires three cells connected in series for such an application. Figure 1.1 [8] shows that a Li-ion system with a graphite-based anode and a LiCoO$_2$ cathode or LiMn$_2$O$_4$ cathode delivers all its capacity above 3V and its single-cell voltage characteristics closely match that of three Ni/MH cells in series. The compatibility of the voltage characteristics can increase the speed of replacement of the Ni/Cd and Ni/MH technologies with the lithium-ion technology in portable equipment applications. Saving two cell cases and associated hardware reduces cost and increases energy density.

For large batteries, for example as required for electric-vehicle (EV), a higher cell voltage is also an advantage as it reduces the number of cells required to achieve the battery voltage. A smaller number of cells reduces the complexity of the battery and its management system.
**Higher Energy Density**

Li-ion batteries provide a higher energy density per unit volume and unit weight than either Ni/Cd or Ni/MH batteries. In addition, their higher voltage and lighter weight contribute significantly to the downsizing, weight reduction and simplified operation of electronic devices. Figure 1.2 [9] shows a comparison of the gravimetric and volumetric energy densities of rechargeable lithium batteries with those of other systems.

![Figure 1.1 Comparison of the voltage profiles of one Li-ion cell with three Ni/MeH cells connected in series. Both cells with LiCoO₂ and LiMn₂O₄ cathodes are shown. Discharge rate is 0.2C [8].](image)

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5
Environment Impact

The impact on the environment of some of the metals is of a major concern, especially when heavy metals are used. For established battery technologies, recycling is a solution. For lead/acid batteries, efficient recycling is in place. For Ni/Cd, some recycling efforts do exist, however costs are high. A Li-ion system with a carbon anode and a lithium manganese oxide cathode requires new recycling methods, but would avoid the heavy metal problem [10].

The rechargeable lithium batteries available commercially today are primarily used in video, cameras and other small devices. In the future, commercial production of rechargeable lithium batteries for large applications such as electric vehicles, load conditioners and domestic robots is likely [11-12].

Figure 1.2 Comparison of the gravimetric and volumetric energy densities of rechargeable lithium batteries with those of other systems [9].
1.2 Fundamentals of the Lithium-Ion Batteries

1.2.1 Classification of Lithium Batteries

The different types of lithium rechargeable batteries identified in Figure 1.3 [13] can be classified conveniently into five categories:

(1). Solid-cathode cells using intercalation compounds for the positive electrode, a liquid organic electrolyte, and a metallic lithium negative electrode.

(2). Solid-cathode cells using intercalation compounds for the positive electrode, a polymer electrolyte, and a metallic lithium negative electrode.

(3). Cells using intercalation compounds for both the positive and the negative electrodes and a liquid or polymer electrolyte (Li-ion cells).

(4). Inorganic electrolyte cells, which use the electrolyte solvent or a solid redox couple for the positive and lithium metal for the negative materials (Li-ion type cells have also been investigated with inorganic electrolytes).

(5). Cells with lithium-alloy anodes, liquid organic or polymer electrolytes, and a variety of cathode materials, including polymers. This technology has been used mainly in small flat or coin cells.
Figure 1.3 Lithium rechargeable batteries (a) with metallic lithium as negative electrode, (b) with lithium alloys or lithiated carbon negative electrode [13].
1.2.2 Structure of the Lithium-Ion Cells

The lithium-ion cells can be designed in any of the typical cell constructions: coin and spirally wound cylindrical constructions. The structures of the coin-type lithium-ion rechargeable batteries are shown in Figure 1.4 [14]. The battery has a current collector for both the positive and negative electrodes to maintain electrical connection, even if the electrode expands and contracts because of charging and discharging.

![Figure 1.4 Structure of coin cell [14].](image-url)
Figure 1.5 [15] shows the structure of cylinder-type lithium-ion battery. The current collectors of the negative and positive electrodes are a thin copper foil and aluminium foil respectively. The electrodes are rolled up in a “jelly-roll” configuration with a polypropylene separator between them. The cell contains a safety vent to release any pressure that may develop if the cell is overcharged or otherwise abused.
1.2.3 Principles of Lithium-Ion Batteries

The advantage of the Li-ion cell is that it uses a lithiated intercalation material for the negative electrode instead of metallic lithium. A lithiated transition metal intercalation compound is used for the positive active material, and the electrolyte is usually an aprotic organic solution.

The cell reaction is:

\[
\text{Li}_y\text{M}_n\text{Y}_m + \text{A}_z\text{B}_w \xrightarrow{\text{discharge}} \text{Li}_{y-x}\text{M}_n\text{Y}_m + \text{Li}_x\text{A}_z\text{B}_w
\] (1-1)

\[
\text{Li}_y\text{M}_n\text{Y}_m \text{ is negative electrode and } \text{A}_z\text{B}_w \text{ is positive electrode. Lithium ions move back and forth between the positive and negative electrodes during charge and discharge [16,17].}
\]

The electrochemical process is the insertion of lithium ions at the negative during charge and their release during discharge, rather than lithium plating and stripping. As metallic lithium is not present in the cell, Li-ion cells are less chemically reactive and should be safer and have a longer cycle life than the cells containing metallic lithium. The reaction mechanism of the Li-ion cell is shown graphically in Figure 1.6 [18] together with the related charge-discharge voltage profile.
Figure 1.6 Model of a lithium-ion battery and of the related charge-discharge voltage [18].
The procedure that evolved for fabricating a Li-ion cell is based on the use of a lithium-rich intercalation compound as the cathode (positive electrode). The cell is assembled by coupling this lithium-rich or lithium-source cathode compound with a lithium-accepting or lithium-sink anode. The cell is “activated” by charging, which transfers lithium ions from the cathode to the anode. Most powdered intercalation compounds are pyrophoric when loaded with lithium. However, lithium will not deintercalate to react with air or moisture if it is sufficiently strongly bound in the intercalation compound. Lithium intercalation compounds are generally air stable when the chemical potential is less than \(-3.5\text{eV}\) [19]. Various examples of Li-ion batteries have been characterised and tested in recent years, but none of them has so far established a technological position in the power source market. This is because they have failed to fulfil one or more of the above crucial requirements; their shortcomings may range from low open-circuit voltage to low energy density, and/or from low rate capacity or poor voltage regulation.

1.2.4 Intercalation Materials

Li-ion batteries rely on intercalation, which is the “reversible insertion of guest atoms into host solid such that the structure of the host is not significantly altered”. If lithium can be intercalated into a host that is not altered by many successive lithium insertions and removals, then this host will probably have good cycle life in electrochemical cells. The amount of lithium that can be intercalated into a host, or its capacity, is as important as the cycle life for practical applications. Much of the present research on Li-ion batteries focuses on finding electrode materials with improved cycle ability and increased capacity for lithium intercalation [20].

The intercalation process involves three principal steps:
(1) Diffusion or migration of solvated \( \text{Li}^+ \) ions.

(2) Desolvation and injection of \( \text{Li}^+ \) ions into the vacancy structure.

(3) Diffusion of \( \text{Li}^+ \) ions into the host structure.

Considering the nature of an electrochemical process, the successful operation of a lithium-ion battery and its effective competition with a pure lithium system require some crucial conditions [18]:

(i) the lithium activity in the negative electrode, \( \text{Li}_y\text{M}_n\text{Y}_m \), must be close to 1 in order to assure open-circuit voltages approaching those obtainable with the pure lithium;

(ii) the equivalent weight of both electrodes must be low in order to assure specific capacity values of practical interest;

(iii) the diffusion coefficient of \( \text{Li}^+ \) ions in the ion-source \( \text{Li}_y\text{M}_n\text{Y}_m \) negative electrode must be high in order to ensure fast charge and discharge rates;

(iv) the changes in Li-ion chemical potential must be small in both electrodes to limit voltage fluctuations during charge and discharge cycles;

(v) both the ion-source and the ion-sink compounds must be easy to fabricate and based on nontoxic compounds in order to ensure low cost and environmental control.

### 1.3 Anode Materials for the Lithium-ion Battery

#### 1.3.1 Lithium Metal Anodes

An attractive feature of metallic lithium is that it has the highest possible specific capacity i.e., 2060 mAh/cm\(^3\) of volumetric capacity and 3860 mAh/g of gravimetric capacity, in addition to the most negative electrode potential (-3.0 V versus SHE) of the alkali metals in appropriate electrolytes. However, cathodic deposition and subsequent anodic dissolution do not achieve 100% efficiency to be achieved [21, 22], so that a
three-fold excess of lithium metal is normally used in order to extend the cycle life of rechargeable lithium cells. This reduces the volumetric and gravimetric specific capacities by a factor of three, i.e., to approximately 690 mAh/cm³ and 1290 mAh/g respectively [23]. These values may be set as a criterion in terms of the specific capacity of alternative materials to metallic lithium.

Over the past 20 years, rechargeable lithium cells have been developed and demonstrated in prototype cells, such as Li/TiS₂, Li/MoS₂, Li/NbSe₃ and Li/MnO₂ [24]. Although some improvements in cycle life and efficiency have been achieved, the limited reversibility of the lithium metal electrode remains a significant problem. The major problems limiting cycle life are short circuiting resulting from the growth of lithium dendrites.

Attempts to cycle lithium metal in liquid organic electrolytes showed that on every cycle some of the lithium plated out on charging and could not be used in the subsequent discharge. In order to avoid a capacity fade, cells were built with a relatively large excess of lithium compared to the stoichiometric amount required for a single cycle.

The average lithium cycling efficiency, E, is defined as shown in the equation 1-2 by:

\[
E = \frac{Q_s - Q_{ex}}{Q_s} / n
\]  

(1-2)

where \( Q_s \) is the amount of lithium stripped, \( Q_{ex} \) is the amount of excess Li, and \( n \) is the number of cycles [25, 26].

Equation (1-2) can also be used to calculate the relative excess \( R = Q_{ex}/Q_s \) of lithium required to achieve a certain cycle number \( n \); \( R = n \times (1-E) \).
The electrolyte favoured in early experiments, LiClO₄ in propylene carbonate, had a typical lithium cycling efficiency of 60\%, thus making R an unreasonably large number for practical cells.

In the twenty years that followed the initial work, a large number of variables that affect \( E \) were investigated and considerable success was achieved in improving it. Many lithium salts were explored and it was found that LiAsF₆ in combination with a variety of solvent systems gives good cycling efficiencies [27]. Solvent systems that received much attention were tetrahydrofuran (THF) and some of its derivatives such as 2-methyl-tetrahydrofuran (2Me-THF)[28], as well as solvent mixtures such as propylene carbonate/ethylene carbonate (PC/EC) [29]. It was realised that certain electrolytes form a so-called solid electrolyte interface (SEI) [30] on the surface of lithium metal. This SEI allows lithium ion transport during charge and discharge but is electronically insulating and protect the lithium metal from further corrosion. In the formation of the SEI, both salt and solvent of the electrolyte play an important role [31-33].

1.3.2 Anodic Carbonaceous Materials

In the past decade there has been much interest in carbon-lithium electrodes to replace metallic lithium in rechargeable batteries. Carbon materials improve the safety of the battery system because the growth of lithium dendrites is eliminated. Carbon is a low cost material for the battery industry. Many different kinds of carbonaceous materials have been developed, such as graphite, coke or carbon fiber materials [34]. At present, the carbon materials show the good performance as anode for lithium ion batteries. The electrochemical intercalation of lithium is described the Eq.1-3 and the faradaic capacity
of the oxidation of the graphite compound fully intercalated by lithium (LiC₆) is 372mAh/g carbon.

\[
6C + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{C}_6
\]  

The specific capacity of lithium is 3860 mAh/g where as the maximum specific capacity that could be obtained from graphite based on LiC₆ is only 372 mAh/g. Clearly, the switch from lithium metal to graphite will result in reduction in the energy density. Hence much effort has been focused on improving the capacity of the carbonaceous anodes during few years. Recently, much higher capacities than the theoretical capacity of graphite have been obtained from heat-treated polyfurfuryl alcohol [35], polyparaphenylene [36] and so on.

The following suggestions for the extra capacity over the theoretical value of 372mAh/g have been proposed:

(i) lithium can occupy nearest neighbour sites [36].

(ii) insertion of lithium species into nanoscopic cavities [37].

(iii) in very disordered carbons containing large fractions of single graphene sheets (like the structure of a house of cards) lithium may be adsorbed on both sides of single layer sheets [38, 39].

(iv) correlating of H/C ratio with excess capacity led to a proposal that lithium may be bound somehow in the vicinity of the hydrogen atoms.

(v) possible formation of multilayers of lithium on the external graphene planes of each crystallite in disordered carbons [40].

(vi) accommodation of lithium in the zigzag and armchair sits [41].
Rechargeable batteries with metallic lithium as anodes can be charged at a rate of C/10 (10 hours for full recharge). In fact, an increase in the recharge current density will enhance the risk of lithium dendrite formation that short-circuit the cell. However, lithium ion cell can be charged effectively in less than two hours [42], as dendrite formation is eliminated by the use of carbon. To reiterate, the unsafe behaviour of the secondary lithium batteries results from the formation of high surface area lithium on the anode with use. Using an Accelerating Rate Calorimeter, Moli Energy Simon Fraser University in Canada, have determined the effect of cycle on the anode stability. Li/MnO\(_2\) AA cells which were cycled 25 times exhibit thermal runaway when heated to 100°C while uncycled cells do not. In contrast, cells with carbon anodes of small surface area show much lower self heating rate which can decrease with cycle life [43]. Concerning the safety issues carbonaceous materials have enormous advantages over lithium.

Two types of carbon with different structure were proposed as anodes in the lithium ion cells. One was a petroleum coke with a disordered structure and the other one was graphite. The structure of graphite is a planar sheet of carbon atoms arranged in a honeycomb.

The planar hexagonal networks of carbon atoms with two different crystalline forms (or phases): hexagonal (2H) and rhombohedral (3R). In the 2H graphite structure, which is the most commonly occurring structure, the carbon layers are arranged in an ABAB sequence, where the B layers are shifted to a registered position with respect to the A layers. In the 3R structure, the stacking sequence is ABCABC, where the C layers are shifted by the same distance with respect to the B layers, as the B layers are shifted with respect to the A layers. A schematic view of these two structures is shown in Fig. 1.7
In both cases, the carbon-carbon distance within the layer is 1.42 Å and the interlayer spacing is about 3.36 Å. The two phases are interchargeable by grinding (2H $\Rightarrow$ 3R) or heating to high temperature (3R $\Rightarrow$ 2H) [45]. However, this phase conversion introduces more turbostratic disorder into the graphite structure, in which the stacking sequence of the graphite of the parallel layers is completely randomized. The increasing disorder also causes a slight enthalpy difference between the 2H and 3R phases, $\Delta H = H_{2H} - H_{3R} = 0.6$ kJ/mol [45]. In other words, the 2H phase in graphite is thermodynamically more stable at normal temperature and pressure than the 3R phase. Due to the small energy difference between the 2H and 3R structures under normal conditions, it is difficult to distinguish between the two phases electrochemically. The voltage difference between the 2H and 3R phases is only about 6mV per mole of graphite. However, the structure difference may be readily detected by X-ray diffraction (RXD) [46].

Carbon material can be used as an anode in lithium-ion cells since the chemical potential of lithiated carbon materials is almost identical to that of metallic lithium as shown in Figure 1.8 [47]. Thus an electrochemical cell with lithiated carbon materials will have almost the same open-circuit voltage as one made with metallic lithium.
Chapter 1. Literature Review

Figure 1.7 Graphite crystal structure; (a) the AB stacking (hexagonal cell) and (b) the ABC stacking (rhombohedral cell) [44].
Figure 1-8 Electrochemical potential of some Li-intercalation compounds vs. Li metal [47].
1.3.3 Anodic Tin-Based Composite Oxides

Recent developments suggest that amorphous metal-oxide materials can be made to work well as anodes for Li-ion batteries. Fujifilm Celltec Co. Ltd. [48], has announced its plans to manufacture and sell new batteries commencing in early 1997, whose anode is an amorphous tin-based composite oxide. This high capacity lithium-storage material in metal-oxide form has been synthesised and claimed it can replace the carbon-based lithium intercalation materials currently in extensive use. The reported gravimetric capacity of tin-based composite oxide (TCO) is greater than 600 mAh/g (0.022 mol of Li per gram), which corresponds in terms of reversible capacity per unit volume to more than 2200 mAh/cm$^3$ (0.075 mol of Li per cubic centimeter). The latter value is about twice the reversible capacity of state-of-the-art high-capacity carbon materials (840 to 1200 mAh/cm$^3$) [49].

1.4 Cathode materials for Lithium-Ion Batteries

By far the largest number of cathode materials that are being combined with a lithium anode to form a rechargeable cell are of the lithium intercalation tape. Currently, three major systems of high voltage cathode materials are available for commercial lithium cells: (i) LiCoO$_2$ by Sony Energytec [50]. (ii) LiNiO$_2$ by Moli Energy [51], and (iii) LiMn$_2$O$_4$ by Bellcore [52]. Both LiCoO$_2$ and LiNiO$_2$ possess a layered structure while LiMn$_2$O$_4$ has a spinel structure. The upper voltage limits of these three systems are in the 4.1 - 4.5V range [53].
1.4.1 LiCoO₂

The lithium cobalt oxide, LiCoO₂, was first described by Mizushima et al. in 1980 [54] and is currently the most extensively used cathode materials for commercial Li-ion batteries. The theoretical capacity of LiCoO₂ is 274 mAh/g. However, due to structural restrictions [55] only a lower amount of lithium may be removed and inserted reversibly. The general consensus between independent researchers is that a maximum of around 150 mAh/g, may be reversibly cycled over many charge-discharge cycles [56]. In most instances groups testing under rates of insertion/extraction consistent with cell usage, report the reversible specific capacities in the range 120-140 mAh/g.

1.4.2 LiNiO₂

LiNiO₂ is one of the three popular cathodes. Although LiNiO₂ has the lowest operating voltage of these three materials, it offers many advantages as a Li-ion cathode material. These include: good high temperature performance; good charge retention; compatibility with a wide selection of electrolyte solutions; ability to cycle over a wide compositional range; environmental friendly and moderately low in cost.

LiNiO₂ has a layered structure in which the lithium and nickel ions are situated in 3(b) and 3 (a) sites respectively [57]. The layered framework provides a two-dimensional path for lithium intercalation and de-intercalation.

LiNiO₂ is more difficult to prepare than either LiCoO₂ or LiMn₂O₄, it needs to be prepared under strongly oxidising conditions. The theoretical capacity of LiNiO₂, assuming 1 Li per NiO₂ unit may be extracted, is about 275 mAh/g. A significantly lower capacity is obtained in actual test cells. However, the overall reversible specific capacities reported for LiNiO₂ are typically 10-30 mAh/g higher than those of LiCoO₂.
1.4.3 LiMn$_2$O$_4$

Lithium manganese oxides as the cathode materials for lithium secondary battery have been studied intensively because they are low-cost, environmental acceptable material [58,59]. These materials are divided into two groups with regard to their potential:

(1). A 4V type such as spinel compounds (space group of Fd3m; Li$_x$Mn$_2$O$_4$, $x \leq 1$) [60]

The cycling of 1 Li per Mn$_2$O$_4$ unit corresponds to a theoretical material utilisation capacity of 148 mAh/g [61]. This figure is lower than the theoretical capacity of the LiCoO$_2$ and LiNiO$_2$. In most experiment cells, it was found that the reversible specific capacity of the 4V range for the LiMn$_2$O$_4$ is about 120 mAh/g, or about 81% of the theoretical capacity. Li/Li$_x$Mn$_2$O$_4$ cells lose capacity gradually when cycled in the 4 V range [62]. This capacity loss has been attributed to several factors [59]:

(i) a gradual dissolution of manganese in the electrolyte solution;

(ii) loss of cathode integrity on deep discharge due to a large volume changes which occur in the spinel lattice when $x \geq 1$ in Li$_x$Mn$_2$O$_4$. These volume changes are a result of the Jahn-Teller distortion of Mn$^{3+}$ cations, which occur when the average manganese valance is approximately 3.5 [63].

(iii) an instability of the electrolyte at the high voltages reached on charge.

Recent work has shown that, when the Mn$^{3+}$-ion concentration in the spinel materials is reduced by the addition of appropriate dopants (Li$^+$, Mg$^{2+}$ or Zn$^{2+}$), improved cycling stability in the 4V range has be achieved[59]. Guohua et al. [64] demonstrated the improved cycling stability of LiMn$_2$O$_4$ doped with Co, Cr and Ni.

Traditionally, the LiMn$_2$O$_4$ compound is made by annealing the corresponding carbonates in the approximate temperature range 700 - 900°C. Other synthesis routes,
primarily using different low temperature method based on sol-gel chemistry, have also been investigated [61].

(2) A 3V type such as spinel-like compounds or a compound which crystallized in an orthorhombic system

Since approximately 1 Li⁺ per Mn₂O₄ unit can be inserted over the approximate 3V voltage plateau, the theoretical capacity of this plateau is roughly the same as the capacity of the 4V plateau, i.e. around 150 mAh/g [64]. However, the delivered capacity is often significantly lower than that of the 4V plateau, and the capacity fade with cycle number is usually greater. It has been reported [65-67] that the electrode impedance increases abruptly at the transition between the 4V and 3V plateau, which then causes lower material utilization and poor cycling properties.

It is concluded [68] that the concurrent cubic to tetragonal phase change which accompanies lithium insertion over this voltage range, confers the inferior electrochemical performance on this materials. The high temperature LiMn₂O₄ spinel compound is synthesized at temperatures greater than 700°C as the 4V type, while the low temperature LiMn₂O₄ spinel-like compound is synthesized at temperatures below 400°C as the 3V type.

1.5 Electrolytes

The electrolyte has a large effect on battery cycling performance [69-70]. Furthermore, the operating temperature and storage characteristics of the batteries depend mainly on the properties of the electrolyte [74-77].
From an electrochemical point of view, the electrolytes must be satisfied with the following requirements [78]:

(i) They must be electrochemically stable, in a voltage window that is at least as wide as the voltage window defined by the electrode reactions. Preferably, the electrolytes should be stable in wider voltage windows in order to accommodate overcharge and discharge reactions.

(ii) They must have sufficient conductivity to allow a reasonable current density. Typically conductivities above 0.1, and more likely greater than 1 mS/cm, are needed at room temperature.

(iii) They must be chemically and electrochemically compatible with electrode materials and other components they may be in contact with in the battery.

(iv) Good thermal stability is also required, especially in contact with the lithium electrode [79].

There are many efforts for developing electrolyte systems suitable for Li-ion batteries. Both Li⁺ conducting polymers and liquid electrolyte solutions have been extensively explored and tested [80]. Ethylene and diethyl carbonates (EC-DEC) as superior solvent system for Li-ion batteries with graphite electrodes have been reported [84]. Graphite electrode can be reversibly cycled (intercalation-deintercalation) at high capacity for hundreds of cycles in Ec-DEC solutions due to the surface films on the electrodes. EC reduction at potentials high above the intercalation potential precipitates (CH$_2$OCO$_2$Li)$_2$ surface films which are compact and efficiently passivate the carbon, avoiding further co-interaction of the graphite with solution species allowing only Li⁺ migration. The stability of these films depends on the salt used. LiPF$_6$ is a good electrolyte for graphite electrodes in EC-DEC mixtures [81].
1.6 Expectations and Limitations of Lithium-Ion Batteries

The present enthusiasm for Lithium-ion batteries is based on the expectation that the use of the Li\(^+\) transfer electrode will lead to improvements in the safety and in the cycle life of lithium rechargeable systems. If these expectations are fulfilled, lithium-ion batteries could soon become viable power sources for a series of popular devices in the field of consumer electronics and appliances. However, lithium-ion batteries have not yet been proposed for commercial scale applications, because the penalties to be paid may still be too high for them to be competitive with other rechargeable batteries. Therefore, the key question is to what extent the lithium-ion electrochemical system innovation will be capable of enhancing the progress of the lithium-ion battery technology. In an attempt to provide some evaluation criteria, some basic characteristics and behaviour of the lithium-ion electrochemical systems are discussed below.

1.6.1 Open-circuit voltage and voltage regulation

One of the main requirements for a successful lithium-ion battery is the proper replacement of the Li negative metal with a Li-insertion compound capable of maintaining the Li\(^+\) activity as close to 1 as possible. In fact, only under this condition, the selected compound exhibit a potential approaching that of the metal and thus give lithium-ion batteries open-circuit voltages approaching those other conventional lithium batteries [82]. The potentials are relative to Li metal and reported for exchange of x Li equivalents per mole.

The variation of potential upon Li\(^+\) exchange is also a crucial factor. Indeed, it is desirable to have a battery which is not only capable of exhibiting a high open-circuit voltage but a small voltage variation upon charge and discharge. In this respect the
choice of lithiated petroleum coke varies as much as 1.5V upon the exchange of the total removable lithium (0<x<0.5) [83]. The voltage fluctuation issue outlined at the initial stage of the lithium-ion battery development, still remains a problem, even in the case of recent generation systems. Indeed, this can be a serious drawback, especially in view of applications in the electronics field where voltage stability is often a priority requirement. Some future attention to the lithium-ion battery development should be devoted to the characterisation of anode materials having not only a lithium activity approaching one in the lithium-rich state, but also a limited change in Li⁺ chemical potential upon lithium exchange.

1.6.2 Specific capacity and energy density

Lithium metal is nearly an ideal electrode material due to its high specific capacity of 3.86 Ah/g. The substitution of Li by any Li-inserted compound inherently leads to sacrifices in capacity. For instance, in the case of LiₓC₆ (x=1), the specific capacity drops to 0.372 Ah/g. These losses in capacity density are directly reflected in losses in energy density.

Fig 1.8 [84] shows theoretical values of energy density (in Wh/kg) related to combinations between a LiₓC₆ (x=0.5) anode and various cathodes. It is clearly seen that even under the best conditions (i.e., using the LiₓC₆ anode in combination with the LiCoO₂ cathode) the maximum achievable energy density is at least 50% lower than that of comparable systems based on Li metal anodes.

Unfortunately, there are no practical ways to overcome this limitation since it is inherent in the choice of any anode as an alternative to lithium metal.
Figure 1.8 Theoretical energy density for electrodic systems based on the combination of Li$_x$C$_6$ (x = 0.5) with various cathode materials. The theoretical energy density of the Li/V$_6$O$_{13}$ couple is also shown for comparison purposes [84].
1.6.3 Rate capacity

Diffusion of Li$^+$ ions within solid materials is an important process in Li-ion batteries. The diffusion kinetics of the Li$^+$ insertion-deinsertion process directly controls the rate of charge and discharge of these batteries. Rate is another consideration in the practical development of lithium-ion batteries. Fortunately, this is not a thermodynamic but a kinetic limitation and thus the problem can possibly be alleviated by selecting proper electrode compositions and morphologies, such as thin-films and large surface areas.

1.6.4 Reversibility and cyclability

Extended cyclability of the lithium-ion batteries requires high reversibility of the electrode processes. Furthermore, it has been ascertained that in systems using Li$_x$C$_6$ anodes, 20% of the initial capacity is inevitably lost due to passivation phenomena and irreversibility of the initial intercalation of Li$^+$ ions into the pristine carbon structure [85]. These facts indicate that the successful operation of Li$_x$C$_6$ anode lithium-ion batteries requires the use of electrode materials capable of providing a large excess of lithium with respect to the faradaic needs.

1.6.5 Safety

This is a very reasonable expectation since the replacement of lithium metal with a lithium-intercalated electrode should reduce the chances of uncontrolled side reactions and other processes which are responsible for the failure and safety incidents experienced with lithium batteries. However, it has to be pointed out that the safety of lithium-ion batteries still remains to be demonstrated in practice. In the case of the
Li₅C₆ anode uncontrolled operations may drive the voltage of the carbon electrode to values at which plating may become the predominant process. In fact, these conditions may very likely occur when the cell is anode limited; attempts to pull out the residual lithium stored in the cathode will inevitable drive the potential of the carbon electrode to values favourable for Li plating, with the risk of building up regions of highly reactive metallic lithium deposited on a finely subdivided carbon surface.

Another concern in establishing the safety of the operation of rocking chair batteries is related to the decomposition of the electrolyte. The organic solutions most commonly proposed as suitable electrolytes for these batteries have ranges of electrochemical stability windows with an upper limit around 4 V vs. Li. The open-circuit voltage of the Li₅C₆/Li₅NiO₂ couple, Li₅C₆/Li₅Mn₂O₄ couple and LiC₆/Li₅CoO₂ couple is 3.9 V, 4.1 V and 4.4 V, respectively. Consequently, under prolonged cycling the cell system may repeatedly assume voltage values much higher than the electrolyte decomposition limit with progressive degradation, possibly accompanied by the building up of gas pressure or of other unsafe side effects. A possible approach is the replacement of the liquid electrolyte with a solid electrolyte. Promising candidates are the Li⁺ conducting polymer electrolytes which are on average characterized by electrochemical stability exceeding 4 V and, in certain cases, even more than 5 V vs Li [86].

1.6.6 Cost

The cost is a parameter which must be taken into consideration when attempting to evaluate the impact that a new system, such as the Lithium-ion battery, may have on the commercial market, is its cost, especially in relation to that of competitive systems such
types of batteries. The compounds used as lithium sources, with the possible exception of carbon, are more expensive than pure lithium. Therefore, the cost of lithium-ion batteries would be higher than that of other lithium batteries. However, it also is expected that the lithium source compounds will be less sensitive to moisture than lithium metal. Consequently, the higher material cost can be offset by a lower assembly cost [87].

As a general conclusion, based on the literature survey one may assume that lithium-ion batteries are expected to be initially more expensive than other lithium batteries. Therefore, the commercial impact of lithium-ion batteries appears to depend on the balance between cost and reliability: only when the cycleability and safety are definitely established, will lithium ion batteries have a chance to compete with the less expensive conventional sources.

1.6.7 Aims of the investigation

The aims of this study were to investigate different anode materials for lithium-ion batteries on a laboratory scale. These materials include in those commercially used carbon-based anodes, recently reported tin-based materials and a conductive ceramic compound. The structure and morphology of those materials were examined by XRD and SEM. The electrochemical properties and cell performance of these anode materials were assessed using test cells.

In the next Chapter, the experimental methods and procedures used in this study are described.
2.1 Chemicals

All the Chemicals used in the present work are listed in table 2.1 and table 2.2.

Table 2.1 Descriptions of Chemicals used for synthesis the anode materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Molecular Formula And weight</th>
<th>Purity</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stannous Oxide</td>
<td>SnO</td>
<td>99+%</td>
<td>ALDRICH</td>
</tr>
<tr>
<td>Stannic Oxide</td>
<td>SnO₂</td>
<td>99%</td>
<td>B.D.H</td>
</tr>
<tr>
<td>Boric Oxide</td>
<td>B₂O₃</td>
<td>99%</td>
<td>SIGMA</td>
</tr>
<tr>
<td>Aluminium Oxide</td>
<td>Al₂O₃</td>
<td>99%</td>
<td>ALDRICH</td>
</tr>
<tr>
<td>Silica</td>
<td>SiO₂</td>
<td>99.8%</td>
<td>ALDRICH</td>
</tr>
<tr>
<td>Lithium Carbonate</td>
<td>Li₂CO₃</td>
<td>99%</td>
<td>ALDRICH</td>
</tr>
<tr>
<td>Tin(II) Pyrophosphate</td>
<td>Sn₂P₂O₇</td>
<td>98%</td>
<td>ALDRICH</td>
</tr>
<tr>
<td>pyrolyzing phnolic resin</td>
<td>C</td>
<td>–</td>
<td>BUEHLER Ltd</td>
</tr>
<tr>
<td>Carbon powder (VXC)</td>
<td>C</td>
<td>–</td>
<td>CABOT Australia Pty.Ltd</td>
</tr>
<tr>
<td>Table sugar</td>
<td>–</td>
<td>–</td>
<td>Australia Market</td>
</tr>
<tr>
<td>Polyurethane foam</td>
<td>–</td>
<td>–</td>
<td>BUEHLER Ltd</td>
</tr>
<tr>
<td>Graphite</td>
<td>C</td>
<td>–</td>
<td>ALDRICH</td>
</tr>
<tr>
<td>Lithium Hydroxide</td>
<td>LiOH</td>
<td>98%</td>
<td>ALDRICH</td>
</tr>
<tr>
<td>Stannic Chloride</td>
<td>SnCl₄</td>
<td>99%</td>
<td>ALDRICH</td>
</tr>
<tr>
<td>Barium Carbonate</td>
<td>BaCO₃</td>
<td>99%</td>
<td>ALDRICH</td>
</tr>
<tr>
<td>Lead Tetroxide</td>
<td>Pb₃O₄</td>
<td>99%</td>
<td>ALDRICH</td>
</tr>
</tbody>
</table>
Table 2.2 Descriptions of chemicals used preparation of electrode and electrolyte

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Molecular Formula &amp; Formula Weight</th>
<th>Purity</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium (hexafluorophosphate)</td>
<td>LiPF$_6$</td>
<td>98%</td>
<td>ALDRICH</td>
</tr>
<tr>
<td>EC (Ethylene carbonate)</td>
<td>C$_3$H$_4$O$_3$</td>
<td>&gt;99%</td>
<td>FLUKA</td>
</tr>
<tr>
<td>DMC (dimethyl carbonate)</td>
<td>C$_3$H$_6$O$_3$</td>
<td>99%</td>
<td>FLUKA</td>
</tr>
<tr>
<td>PVDF (polyvinylidene fluoride)</td>
<td>(-CH2CF2-)$_n$</td>
<td>_</td>
<td>ALDRICH</td>
</tr>
<tr>
<td>DMP (dimethyl phalate)</td>
<td>C$_6$H$_4$-1,2-(CO$_2$CH$_3$)$_2$</td>
<td>99%</td>
<td>ALDRICH</td>
</tr>
</tbody>
</table>
2.2 Experimental Procedures

The whole experimental procedure is illustrated in Fig. 2.1, and each part of the procedure will be described in the following subsections.

Fig. 2.1. Schematic diagram of experimental procedures.
2.3 Materials Preparation

Two types of anode materials were synthesised. The preparation of tin-based composite oxide and carbonaceous materials will be described in chapter 3 and chapter 4 respectively.

2.4 Electrode/Cell Fabrications

Electrodes and cells are fabricated by following procedures.

(1) Electrode Fabrication

The electrode materials were ground at a rotation speed of 125rpm for 30 minutes with a Fritsch Planetary Mill (Pulverisette 5 manufactured in Germany). Electrodes were prepared by coating slurries of the respective powders and Polyvinylidene fluoride (PVDF) dissolved in dimethyl phalate (DMP) on a stainless steel net substrate. The thickness of the coated film was about 300μm. After coating, the electrodes were dried for 12 h at 120°C and pressed between steel plates at 3.0×10^6 Pa/cm². The area of electrode was 0.785 cm².

(2) Cell assembly

The structure of the Teflon test cells is shown in Fig. 2.2. The test cell consisted of two stainless lips, Teflon case and a spring. The spring was used to connect two terminals. The cells used a polypropylene microporous separator, the separator was sandwiched between both electrodes. An electrolyte [1M LiPF₆ dissolved in a 50:50 volume percent (v/o) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC)], and a 300μ thick, 0.78 cm² lithium foil for the negative electrode were used. Cells were assembled
in an argon-filled glove box (Unilab, Mbraun, USA) with both water and oxygen concentrations less than 5ppm.

Fig. 2.2. Structure of Teflon test cell.
2.5 Electrochemical testing

2.5.1 Charge/discharge of cells

Charge/discharge tests were carried out by using a battery test device (DC-5, Shanghai Zhen Fang Electronic Co. China) with a computer (PC-486) and software. The system is capable of switching between charge and discharge automatically according to the cutoff potentials set. All cells were tested at a constant current of 0.125 mA/cm². The battery charge/discharge system is schematically illustrated in Fig. 2.3.

![Fig. 2.3. Schematic of charge/discharge system.](image)

2.5.2 Cyclic voltammetry

The basic approach in controlled-potential methods of electrochemistry is to control in some manner the potential of the working electrode while measuring the resultant current, usually as a function of time. In cyclic voltammetry, the voltage is an scanned
from $E_1$ to $E_2$, then is reversed from $E_2$ to $E_1$. Fig. 2.4 illustrates the potential-time profile used for cyclic voltammetry.

![Diagram](attachment:image.png)

**Fig. 2.4. Potential-time profile used for cyclic voltammetry.**

Cyclic voltammetry is one of the most reliable electrochemical approaches to elucidate the nature of the electrochemical process, and to provide insights into the nature of processes beyond the electron-transfer reaction. It is used in the present work to study the electrochemical properties and estimate the cycle efficiencies. In the cyclic
voltammogram, the positive current represents the lithium de-intercalation process, and negative current is the lithium intercalation process. Data were acquired using a scanning potentiostat (362 Model, EG&G Princeton Applied Research or/and CV-27, AD Instruments Pty.Ltd.) with a Maclab/8 interface (Analog Digital Instruments, AD Instruments Pty. Ltd.) to a Macintosh computer supported by Chart version 3.3.5 software. The system is schematically illustrated in Fig. 2.5.

Fig. 2.5. Schematic of electrochemical measurement system.
2.5.3 **Electrochemical AC impedance analysis**

Impedance spectroscopy (IS) is a powerful method of characterising many of the electrical properties of materials and their interfaces with electronically conducting electrodes. Its application in the mechanistic study of electrochemical processes has expanded rapidly over the last two decades and has proved to be a powerful experimental method for the study of surface processes. It is applied in the present work to study the discharge mechanism of the negative electrodes of lithium-ion batteries.

Impedance analysis was conducted using an EG&G PARC Model 6310 Electrochemical Impedance Analyzer manufactured by Princeton Applied Research. The analyzer is equipped with Model 398 software. The whole system applies an ac excitation to an electrochemical system, measures the response of the system to the excitation, and digitizes and stores the resulting data for processing and display. The frequency of the ac excitation ranges from 50µHz to 100kHz.

2.6 **Sample Powder Surface Area Measurement**

A particle size analyzer (Mastersizer with a computer) characterises the surface areas of the samples. The Mastersizer (MSS Model, Malvern UK) is equipped with Mastersizer operating software.

Particle size analyser normally will only give a particle size distribution and average size, however, a specific surface area under a spherical particles assumption can be calculated by the software (Mastersizer Software) and these results are expressed in terms of equivalent spheres and can be used as reference data only.
2.7 X-Ray Diffraction (XRD)

X-ray diffraction was performed on a Philips PW1010 X-ray diffractometer (Holland). The instrument operates at room temperature, with 0-2θ optics and is equipped with a 3kW generator and various X-ray tubes (Cu, W, Mo, Cr, and LiCoO₂). The instrument is fully automated and operates in conjunction with a comprehensive data (ICDD, US). The 2θ accuracy of the instrument is ±0.005 degree. The system is interfaced with Sietronics XRD 122 and an advanced TRACE version 3.0 software designed for graphical processing and manipulation of XRD traces, or scans (provided by Diffraction Technology Pty. Ltd). The target material and filter were selected to be Cu (Kα₁=1.54 Å) in the present work. The tube voltage and current were 40 kV and 25 mA respectively.

2.8 Scanning Electron Microscopy (SEM)

Morphologies of the electrodes were examined using a Leica Model Stereoscan 440 scanning electron microscope manufactured in the UK. The instrument is fully automated and software controlled (beam control, XYZ stage control, etc.). It is equipped with a secondary electron detector and backscattered electron detector. At the highest magnification, the resolution is in the nanometers range. SEM examinations were carried out at room temperature under an accelerating voltage of 20 kV.
Chapter 3.
Tin-Based Oxide Composites As Anode Materials For Lithium-Ion Batteries

3.1 Introduction

The tin-based composite oxide (TCO) material has a basic formula represented by SnMₓOᵧ, where M is a group of glass-forming metallic elements whose total stoichiometric number is equal to or more than that of tin (x≥1) and is typically comprised of a mixture of B (III), P (V), and Al (III). In the oxide structure, Sn (II) forms the electrochemically active center for Li insertion and potential development, and the other metal group provides an electrochemically inactive network of (M–O)–bonding that delocalises the Sn (II) active center. To confer high reversibility in Li storage and release, the Sn-O framework was thus anisotropically expanded by incorporating glass-forming network elements B, P, Al. The Li-ion mobility is enhanced in the anisotropic glass structure, which is favourable for ionic diffusion and release[88].

The reaction mechanism of lithium with SnC₂, SiSnC₃, and Li₂SnO₃ was proposed to follow a two-step process [89]. Using SnO₂ as an example, firstly lithium is introduced forming a Li₂O and Sn. The breakdown of the SnO₂ into Li₂O and Sn is for the most part irreversible.

\[ 4 \text{Li} + \text{SnO}_2 \rightarrow 2\text{Li}_2\text{O} + \text{Sn} \]  \hspace{1cm} (3-1)
Then, a further 4.4 Li atoms per mole react to form Li_{4.4}Sn.

\[ 4.4\text{Li} + \text{Sn} \leftrightarrow \text{Li}_{4.4}\text{Sn} \]  

(3-2)

Li alloys with Sn which is almost reversible.

The following factors are responsible for good charge-discharge capacity retention[89].

(1) the grains which make up the particles of the material should be as small as possible. Then, regions of tin which form are kept small and enable the two-phase coexistence regions between bulk Li-Sn alloys of different composition do not occur.

(2) the particles themselves should be small so that they can each be well contacted by carbon black during electrode manufacture.

(3) the voltage range of cycling must be selected so that the tin atoms do not aggregate into large regions which grow in size. This aggregation can be identified by the growth of peaks in the differential capacity vs. voltage data as a function of cycle number.

Fig. 3.1 schematically illustrates the reaction mechanism that occurs in the tin oxides and tin oxide composites. In the diagram SnO_2 is assumed to be the starting material, but this could be easily replaced by any other starting materials by simply adjusting the stoichiometry of the added lithium. Lithium reacts with SnO first to form a Li_2O "matrix-glue" and Sn (refers to equation 3-1). The matrix helps to hold the Li-Sn regions together through the large volume changes in the subsequent alloying/dealloying process by resisting crumbing under the large volume changes in the process. The breakdown of the oxide into Li_2O and Sn is for the most part irreversible. The further insertion of lithium to LiSn involves the formation of lithium layered structures and that these structurally related phases could be considered to be lithium intercalates. Further
lithium insertion through to Li$_{22}$Sn$_5$ was considered the insertion of lithium into unlayered structures together with large volume increases.

Better cycle life should be obtained if higher voltages (above 1.0 V) and lower voltages (near 0 V) are avoided [89]. The choice of upper the cut-off voltage appears to be most significant. If the cut-off is too high (above 0.8V), then Sn itself may be formed. If the cut-off if even higher (>1.3V), the Li$_2$O matrix holding the Sn atoms may be destroyed. The formation of Sn may create problems because Sn is ductile and has a low melting point, suggesting good atomic mobility at room temperature. By contrast, the Li-Sn alloy phases all have higher melting points than tin and are more brittle. Thus, charging to the limit of metallic tin (above 0.8V) may aid the Sn aggregation process. Once the aggregates grow too large, then two-phase regions are observed, along with volume mismatch, resulting in capacity fade [89].

In this chapter, studies were performed on Sn$_{1.0}$B$_{0.56}$P$_{0.40}$Al$_{0.42}$O$_{3.6}$, Li$_2$SnO$_3$, SiSnO$_3$ and SnO$_2$ following the newly reported results. The synthetic methods of those tin-based oxide and composites, the electrochemical properties and the structures of these materials were investigated.
Fig. 3.1. Reaction mechanism schematic for reaction of lithium with tin(IV) oxide[89].
3.2 Materials Synthesis

Samples of $\text{Sn}_1\text{B}_{0.56}\text{P}_{0.40}\text{Al}_{0.42}\text{O}_{3.6}$, $\text{Li}_2\text{SnO}_3$ and $\text{SiSnO}_3$ were synthesised by using a Lindberg tube furnace as described in chapter 2. Two kinds of stannic oxide have been used, one was a commercially available product and the other was prepared by a sol-gel method.

(1) Synthesis of $\text{Sn}_1\text{B}_{0.56}\text{P}_{0.40}\text{Al}_{0.42}\text{O}_{3.6}$

Powders of $\text{SnO}$, $\text{B}_2\text{O}_3$, $\text{Sn}_2\text{P}_2\text{O}_7$, and $\text{Al}_2\text{O}_3$ were mixed and ground at a molar ratio of $\text{Sn}:\text{B}:\text{P}:\text{Al}=1.0:0.56:0.4:0.42$. The powder mixture was added into an alumina crucible and the crucible was inserted into a tube furnace. The powder mixture was then heated in a rate of 10 °C/min from the room temperature to 1100 °C and held at that temperature for more than 10 hours under flowing argon to invoke the reaction in a molten state. The resulting product was then quenched to room temperature to yield a transparent yellowish glass. The glassy material has the nominal composition $\text{Sn}_1\text{B}_{0.56}\text{P}_{0.40}\text{Al}_{0.42}\text{O}_{3.6}$.

(2) Synthesis of $\text{Li}_2\text{SnO}_3$

Equimolar amounts of $\text{Li}_2\text{CO}_3$ and $\text{SnO}_2$ were dry-blended, heated in an alumina crucible in the tube furnace at a heating rate of 10 °C/min from the room temperature to 1000 °C and then held at the temperature for 7 hours in air, and cooled slowly to room temperature. The resultant white powder was ground in a ball-mill for 20 min.

(3) Synthesis of $\text{SiSnO}_3$

Equimolar amounts of $\text{SnO}$ and $\text{SiO}_2$ were dry-blended and heated in an alumina crucible in a tube furnace. The powder mixture was heated at a heating rate of 10 °C/min from the room temperature to 1000°C and then held at the temperature for 12
hours under flowing argon, and then quenched to room temperature. The resultant product was yellow glassy SnSiO$_3$ and formed a white powder after grinding.

**4) SnO$_2$ preparation by sol-gel method**

A sol-gel method was used to prepare a fine powder of SnO$_2$. It is a simple route for preparing fine powders on a nanometer scale and with homogenous particle size. SnCl$_4$·5H$_2$O was dissolved in distilled water. LiOH aqueous solution was added until the pH value reached 9. A milky-white Sn(OH)$_4$ gel was formed following the reaction:

\[
\text{SnCl}_4 + 4\text{LiOH} \rightarrow \text{Sn(OH)}_4 + 4\text{LiCl} \quad (3-3)
\]

The gel was washed with distilled water to remove Cl$^-$ and Li$^+$ ions. After drying and calcining at 1000°C in air for 4 hours, a white powder of SnO$_2$ was obtained.

**3.3 X-ray diffraction Analysis**

X-ray diffraction analysis for the powders of Sn$_{1.0}$B$_{0.56}$P$_{0.40}$Al$_{0.42}$O$_{3.6}$ and SiSnO$_3$ established the noncrystalline (amorphous) structure of glassy materials. Figs. 3.2 and 3.3 shown the X-ray patterns. A broad band of weak diffraction was observed, peaking at around $2\theta = 27$ to $28^\circ$, without concomitance of any diffraction line assigned to crystalline forms. The diffraction patterns of Li$_2$SnO$_3$, and SnO$_2$ in Figs. 3.4 and 3.5 agree with those reported in the literature [90].
Fig. 3.2. The powder x-ray diffraction pattern of $\text{Sn}_{1.0}B_{0.56}P_{0.40}Al_{0.42}O_{3.6}$. 
Fig. 3.3. The powder x-ray diffraction pattern of SiSnO$_3$. 
Fig. 3.4. The powder x-ray diffraction pattern of Li₂SnO₃.
Fig. 3.5. The powder x-ray diffraction pattern of SnO$_2$. 

Chapter 3. Tin-Based Oxide Composites As Anode Materials For Lithium-Ion Batteries
3.4 Charge/discharge Characterisation

Electrodes using the above materials were prepared by coating slurries of the respective powders (85% by weight), carbon black (10% by weight), and polyvinylidene fluoride (PVDF) (5% by weight) dissolved in (D.M.P) on a stainless steel net substrate. All cells were assembled in an argon-filled glove box. Details of the test cell assembly were already described in the section 2.4.

All cells were cycled between 0.2-1.3V at a constant current of 0.125 mA/cm². Fig. 3.6 shows the discharge capacity vs the cycle number for cells made from four different samples. The discharge capacity of SnO₂ was the highest while the capacity of Sn₁.₀B₀.₅₆P₀.₄₀A₁₀.₄₂O₃.₆ was lowest at the first three cycles, however its capacity was not appreciably reduced after that compared with others.

Fig. 3.7 shows a comparison of the capacities for two kinds of SnO₂. The capacity of SnO₂ prepared by the sol-gel method is much higher than that of the SnO₂ without the sol-gel treatment. This is due to that much finer particle size and homogeneous particle size distribution have been obtained through the sol-gel treatment [91].
Fig. 3.6. Capacity vs. cycle number for different samples, cycled between 0.2-1.3V at a current density of 0.125 mA/cm$^2$. 
Figure 3.7 Capacity vs. cycle number for cell of two kinds of SnO$_2$, cycled between 0.2-1.3V at a current density of 0.125 mA/cm$^2$. 
3.5 Effects of the Voltage Range on the Capacity Retention of SnO₂

Fig. 3.8 shows that the capacity retention is improved when the voltage ranges is reduced. Better cycling was obtained at the voltage range between 0.3-1.0V. When the voltage range was between 0.0 and 1.3V, the rate of capacity decline increased dramatically. It is clear that the material shows sensitivity to the choice of the voltage cut-offs.

In order to quantify the cycling stability of the samples, the capacity retention index, $R_{10/1}$, is used. This is the capacity of the tenth charge cycle divided by that of the first charge cycle. Cells that are cycling well should have $R_{10/1}$ close to one.

Table 3.1 lists the $R_{10/1}$ value for SnO₂ at different voltages.

<table>
<thead>
<tr>
<th>Voltage cut-offs</th>
<th>Capacity Retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2, 1.3V</td>
<td>$R_{10/1} = 0.54$</td>
</tr>
<tr>
<td>0.2, 1.0V</td>
<td>$R_{10/1} = 0.83$</td>
</tr>
<tr>
<td>0.3, 1.0V</td>
<td>$R_{10/1} = 0.95$</td>
</tr>
</tbody>
</table>
Fig. 3.8 Discharge capacity vs. cycle number for SnO\textsubscript{2} at different voltage cut-offs at a current density of 0.125 mA/cm\textsuperscript{2}.
Chapter 3. Tin-Based Oxide Composites As Anode Materials For Lithium-Ion Batteries

3.6 Cyclic Voltammetric (CV) Measurement

CV tests on the Sn$_{1.0}$B$_{0.56}$P$_{0.40}$Al$_{0.42}$O$_{3.6}$ electrode were carried out in a three electrode testing cell at a scan rate of 0.1mV/s at 25 °C. Lithium metal was used as both the counter and reference electrodes. The CV curves of Sn$_{1.0}$B$_{0.56}$P$_{0.40}$Al$_{0.42}$O$_{3.6}$ are shown in Fig. 3.9.

In the first cycle a reduction peak (a) is seen at about 1.3V, corresponding to the formation of the matrix Li$_2$O and Sn, and this is completely irreversible. The second reduction peak (b) is seen near 0.1V and this reduction peak is reversible during subsequent cycles. The reduction peak near 0.1V corresponds to that Sn alloys with Li. In the positive sweep an oxidation peak (c) is seen at 0.6V, which indicates that Li$^+$ ions will be de-intercalated at such a low voltage. The decay of the peak current with cycling is not significant which implicates a good cycling reversibility of the electrode. This is in agreement with the cycling-test results of Fig. 3.6.
Fig. 3.9. Cyclic voltammetry of Sn$_{1.0}$B$_{0.56}$P$_{0.40}$Al$_{0.42}$O$_{3.6}$

at a scan rate of 0.1mV/s.
3.7 Electrochemical Impedance Spectroscopy (EIS) studies

Impedance analysis was performed on a three electrode test cell. The working electrode was the $\text{Sn}_{1.0}\text{B}_{0.56}\text{P}_{0.40}\text{Al}_{0.42}\text{O}_{3.6}$. Both the counter electrode and reference electrode were lithium.

The impedance behaviour of an electrode system, i.e. an impedance plot in either Nyquist form (or in Bode form or others), mainly depends on two properties of the system: (i) the electrochemical double layer and (ii) the so-called faraday contribution. These properties are influenced by variables such as the electrode potential, the surface concentrations of the reactance, temperature of the electrolyte, layer thickness and conductivity surface roughness etc.

In this study, the test cell was discharged under the constant potential control condition, i.e., the potential of the working electrode of the test cell was stepped from the open circuit potential (OCV) to 0.8 V, 0.4 V and 0.02 V consecutively. In each discharge state, before starting the impedance measurement, the test cell was held at the given discharge potential for a long period of several hours until the discharge current was negligible ($<1\mu\text{A}$). For the $\text{Sn}_{1.0}\text{B}_{0.56}\text{P}_{0.40}\text{Al}_{0.42}\text{O}_{3.6}$/solution interface, the equivalent circuit was suggested as follow:

![Equivalent circuit](image)

**Fig. 3.10. Equivalent circuit of the Sn$_{1.0}$B$_{0.56}$P$_{0.40}$Al$_{0.42}$O$_{3.6}$ electrolyte interface**
Where $R_e$ is the electric resistance of the electrolyte, $C_f$ and $R_f$ are the capacitance and the resistance of surface films formed on the sample and current collector, respectively., $R_{ct}$ is the charge transfer resistance, $Z_w$ is the Warburg impedance and $Z_{cpe}$ is the constant phase element. The constant phase element is introduced to represent the depressed semicircle in the middle frequency region. An origin of the presence of a constant phase element in the present electrochemical system may be attributed to the irregular morphology of the electrode. However, detail interpretation of the $Z_{cpe}$ is beyond of this work and therefore is not discussed in this study.

The experimental data presented in Nyquist form were given in Figs. 3.11-3.13. A computer simulation software (EQUICRT, version 4.51) was applied to those experimental data based on the proposed model and the corresponding simulated results were also included in those Figs. The simulation results were a good fit to the experimental data. Calculated results based on the equivalent circuit are listed in Table 3.1.

Table 3.1 Parameters of the $\text{Sn}_{1.0}\text{B}_{0.56}\text{P}_{0.40}\text{Al}_{0.42}\text{O}_{3.6}$ system at different discharge States.

<table>
<thead>
<tr>
<th>Discharge potential (V)</th>
<th>$R_e$ (Ω)</th>
<th>$R_f$ (Ω)</th>
<th>$C_f$ (F)</th>
<th>$Z_{cpe}$ (1/Ω)</th>
<th>$n$</th>
<th>$R_{ct}$ (Ω)</th>
<th>$Z_w$ (1/Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>1.82</td>
<td>322.6</td>
<td>3.97E-6</td>
<td>1.34E-5</td>
<td>1.0</td>
<td>23.4</td>
<td>5.87E-4</td>
</tr>
<tr>
<td>0.4</td>
<td>2.85</td>
<td>298.1</td>
<td>1.218E-6</td>
<td>5.52E-4</td>
<td>0.193</td>
<td>2090.8</td>
<td>3.227E-4</td>
</tr>
<tr>
<td>0.02</td>
<td>0.775</td>
<td>7.902</td>
<td>1.054E-4</td>
<td>3.78E-2</td>
<td>0.112</td>
<td>13.64</td>
<td>1.39E-1</td>
</tr>
</tbody>
</table>
Data from Table 3.1 show that the resistance of the passivating surface films, $R_f$, decreases during the discharge (lithium ion insertion) and this change is more significant while discharging around 0.02 V. However, the charge transfer resistance, $R_{ct}$, increases significantly while discharging from 0.8 V to 0.4 V and then decreases while discharging at 0.02 V. The mechanism for such a dramatic increase in $R_{ct}$ is unknown at the stage. However, this could be explained by that at near 0.8 V the lithium de-intercalation process occurred at the electrode, which could relate to the $R_{ct}$ at this state. At the near 0.02 V the lithium intercalation process occurred at the electrode, which could relate to the $R_{ct}$ of the electrode at this state. At the near 0.4 V either the lithium intercalation or de-intercalation process was proceeding rather slowly compared to the other two situations. Those observations are in good agreement with the CV measurement results and confirms that the lithium ion intercalation into the TCO electrode happens at a lower potential.
Fig. 3.11 Nyquist plot of the electrode system at 0.02 V (vs. Li/Li⁺).
Fig. 3.12 Nyquist plot of the electrode system at 0.4 V (vs. Li/Li⁺).
Fig. 3.13 Nyquist plot of the electrode system at 0.8 V (vs. Li/Li\(^+\)).
3.8 Summary

From the results and discussion given above, it can be concluded that:

1. Tin oxide composites represent a new class of material for the anode of Li-ion cells. The capacity of SnO$_2$ (over 400mAh/g) is higher than other materials tested.

2. A sol-gel method has been used to prepare SnO$_2$ powder. The capacity of SnO$_2$ electrodes prepared by the sol-gel method is much higher than that of SnO$_2$ without the sol-gel treatment.

3. The capacity retention is improved as the voltage cut-offs were selected appropriately. Better cycling performance was obtained at a voltage range between 0.3V and 1.0V for the SnO$_2$ anode material.
Chapter 4. Carbon Materials As Anodes For Lithium-Ion Batteries

4.1 Introduction

Since the first rechargeable lithium-ion battery was reported in 1990 [92] consistent attention has been devoted to this novel type of lithium battery in which the lithium anode or lithium-accepting anodes are replaced by carbonaceous anodes - lithiated carbonaceous materials. Many different kinds of carbonaceous materials have been developed, including graphite-type, hard carbon-type and soft carbon-type materials, and some of them are currently used for commercially available lithium-ion batteries.

It is known that a maximum of one lithium atom per six carbon atoms can be intercalated when lithium is fully intercalated into graphite, the intercalated lithium exists as a screened ion between two adjacent graphite layers, the theoretical specific capacity of LiC₆ is 372mAh/g.

Some carbonaceous materials have been reported to present specific capacities of about twice that of the theoretical limit capacity of LiC₆ [93, 94]. Some commercial products present a superior cycle-life performance, however, their reversible capacities and the rate capacity seem to be lower [95, 96]. The irreversible capacity of carbon/graphite electrodes is defined as the difference in capacity between the first discharge and the subsequent charge. In the commercial Li-ion cell, to compensate for the irreversible capacity of the anode, excess cathode material is required, which detracts from its overall energy density and adds significantly to the cell's cost. Therefore, the
irreversible capacity of the anode for lithium is a critical parameter which must be minimized [97, 98].

In order to reduce the irreversible capacity, different methods have been explored. These include the chemical or electrochemical inserting lithium ions into carbon/graphite materials prior to assembly of the Li-ion cell [99, 100] and the incorporation of Li-ions soluble in the precursor [101].

Over hundred different kinds of carbonaceous materials with variety properties for different purposes can be found in the market. It is not clear and also difficult to decide which kind of carbonaceous material is the most suitable for the lithium-ion batteries.

In the present study, five different kinds of carbonaceous materials were for the convenience of preparation, their typical carbonaceous structures and availability. The structure and morphology of those materials were also investigated. A pre-lithiation treatment was applied to the pyrolyzed sugar carbon to explore the effect of this treatment on the electrochemical properties, particularly, on the irreversible capacity of the electrode.

### 4.2 Material Synthesis

Five types of carbon or graphite materials were used in this study which include:

1. Glassy carbon (GC) - prepared by pyrolyzing phenolic resin precursor.
2. Polyurethane carbon (PU) – prepared by pyrolyzing polyurethane foam.
4. Carbon black (VXC) – (provided by Cabot, Australia Pty. Ltd).
5. Graphite powder (GP) - (provided by Aldrich, Ltd).
Sample disks of pyrolyzed phenolic resin with a thickness of 0.25 cm and a diameter of 2.5 cm were obtained by curing at 160 °C/3000 P.S.I. for 5 minutes with a Montersimliment 3 (Buehler Ltd. USA). Bulk PU samples (sponge), available from the laboratory, were cut into a suitable size to fit into a crucible then put in the tube furnace for further treatment. Table sugar (commercially available from Franklins) underwent a "dewatering" process before further treatment. The first three carbon materials were prepared using a two-stage carbonization procedure, i.e. the pre-carbonization treatment and the carbonization procedure, by using an automatic temperature control oven (Ceramic Engineering, Sydney Australia) and a tube furnace (Ceramic Engineering, Sydney Australia). The last two materials were commercial available graphite powder (GP) and carbon black (VXC), which were used for the electrode fabrication without further treatment.

(1) Pre-carbonizing process:

First, pyrolyzing phenolic resin and pyrolyzing polyurethane foam precursor were weighted and put in a ceramic (Al₂O₃) boat. The pre-carbonizing process was then carried out in air from room temperature to 230 °C at a slow heating rate of 10 °C/hour and then held at 230 °C for a long annealing period of 18 hours in an oven. The pre-carbonizing process is necessary and important for the carbonizing of a precursor in order to obtain a stabilised and dense product. To obtain a dense carbon with the smallest possible pore size, a low heating rate and a long annealing time are preferred.
(2) "Dewatering" process

A "dewatering" process was applied only to the table sugar precursors. Sugar precursor contained in a beaker was heated in an oven controlled at 190 °C for 20 hours during which the sugar melted, decomposed and partially carbonized. After the "dewatered" sugar char obtained had solidified, it was used as a precursor for further high-temperature pyrolysis.

(3) Pyrolyzing process (carbonization)

After the pre-carbonizing process, sugar precursors were heated in a tube furnace under flowing argon atmosphere at a heating rate of 60 °C/hour from room temperature to a number of pyrolyzing temperature ($T_{pyr}$) and soaked at the $T_{pyr}$ for 2 hours. The optimum pyrolyzing temperature of 1050 °C for phenolic resin (PR) and polyurene (PU) was chosen based on the results of previous work [102].

Table sugar has long been used as a precursor to produce carbon because of its availability, chemical purity, low cost and reproducibility during carbonization processes. In this study, pyrolyzed sugar carbon was chosen because it is a typical hard carbon and has been demonstrated to present specific capacities of about twice that of the theoretical limit capacity of LiC$_6$ in the Li-ion cell.

4.3 Characterisation of the Carbon Anode Materials

4.3.1 X-ray Diffraction

Powder XRD measurements were performed on these carbonaceous materials. Figs 4.1 (a – c) show the XRD patterns for GC, PU, and VXC, respectively. All the peaks have
a broad shape indicating highly disorder carbons. Fig. 4.1(d) shows the typical pattern of graphite, which indicates a highly crystalline graphite.

![Graph of X-ray diffraction patterns for materials of Glass carbon, PU carbon, black carbon and Graphite](image)

**Fig. 4.1.** X-ray diffraction patterns for materials of Glass carbon, PU carbon, black carbon and Graphite
4.3.2 Lithium/carbon Cell Cycling

All cells were discharged and charged between 0-2V at a constant current of 0.125 mA/cm². The cells had a plateau at 0.8V during the first discharge cycle. However, in the subsequent discharge cycles these plateaus were not observed, as shown in Fig. 4.2. This means that some electrochemical reactions occur only during the first discharge process. Fong et al [103] attributed this to the formation of a passivating layer on the carbon surface.

Table 4.1 Results of the charge/discharge tests for the carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m²/g)</th>
<th>Discharge capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>first</td>
<td>fifth</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.19</td>
<td>495.8</td>
</tr>
<tr>
<td>VXC</td>
<td>0.68</td>
<td>785.4</td>
</tr>
<tr>
<td>GC</td>
<td>0.32</td>
<td>401.4</td>
</tr>
<tr>
<td>PU</td>
<td>0.49</td>
<td>522.8</td>
</tr>
</tbody>
</table>
Fig. 4.2. Discharge profiles of samples at a current density of 0.125 mA/cm²:

(a) glass carbon (GC), (b) PU carbon, (c) VXC and (d) graphite powder.
According to the discharge curves shown in Fig. 4.2 (d), the first discharge profile for the graphite had a narrow plateau around 0.8V and a larger plateau around 0.25V. The other samples had a similar discharge profiles with large plateaus around 0.8V and the subsequent discharge profiles were steeper than that of graphite. The shape difference in the discharge profiles shown in Fig. 4.2. can be explained by the different structure of those samples. Samples of GC, PU and VXC show a typical amorphous structure that is distinguished with a typical crystal structure of graphite powder. So that the staged phase formed during the lithiation observed at the graphite [104] is almost undistinguishable. The discharge capacities of all four samples are recorded in the table 4.1. Among those data, the graphite shows the highest capacity of above 300mAh/g.

Fig. 4.3 shows the charge capacities of the carbon and graphite samples. In order to quantify the cycling stability of the different samples, the capacity retention index can be used [105]. $R_{10/1}$, is the capacity of the tenth charge cycle divided by the capacity of the first charge cycle. The results of the capacity retention index are listed in the table 4.2. Cells that are cycling well should have $R_{10/1}$ close to one. The glass carbon (GC) shows lower capacity, but the capacity retention index is close to one, indicating the good cycling behaviour.
Fig. 4.3 Discharge capacity of the carbon electrodes at a discharge current density $0.125 \text{ mA/cm}^2$. 
Chapter 4 Carbon Materials as Anodes for Lithium-Ion Batteries

Table 4.2 The capacity retention index of carbon materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tenth charge capacity (mAh/g)</th>
<th>First charge capacity (mAh/g)</th>
<th>Capacity retention index ($R_{10/1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>150</td>
<td>153</td>
<td>0.98</td>
</tr>
<tr>
<td>PU</td>
<td>121</td>
<td>218</td>
<td>0.55</td>
</tr>
<tr>
<td>VXC</td>
<td>170</td>
<td>192</td>
<td>0.88</td>
</tr>
<tr>
<td>Graphite</td>
<td>234</td>
<td>261</td>
<td>0.89</td>
</tr>
</tbody>
</table>

4.3.3 Cyclic Voltammetric Measurements

Cyclic Voltammetry (CV) of the carbon electrode was carried out in the range 0 to 2.0 V vs. Li/Li$^+$ at a scan rate of 0.1 mV/s. Fig. 4.4 shows the CVs of the VXC electrode. In the initial cathodic sweep (to 0 V vs Li/Li$^+$), two reduction peaks, $a$ and $b$, are observed at near 0.6 V and 0 V respectively. In the second and subsequent cycles, the 0.6 V peak disappears. This phenomenon indicates that (i) a passivating layer could be formed or (ii) lithium reacts with surface function groups and this is irreversible. The CV results also indicate that lithium intercalates into VXC carbon below 1.1 V. Upon the anodic sweep, the charge (lithium de-intercalation) capacity is low in the early cycles and gradually increase during subsequent cycles. The broad current peaks reveal their non-graphitized structures. Fig. 4.5 shows the CVs of graphite electrode. The higher anodic peaks compared with that of VXC indicate the kinetics of lithium
intercalation/de-intercalation in the graphite to be faster than that of VXC. This may be attributed to better conductivity and the crystal structure of the graphite. Two peaks, b and c, are found after subsequent cycles (about 10). This is attributed to the lithium plating, peak b, and the dissolving of lithium (peak a) happened to the graphite electrode, due to the low discharge cut-off voltage used (0V, vs Li/Li⁺). However, this does not happen to the VXC electrode.

![Cyclic voltammograms of VXC in 1 M LiPF₆ at a sweep rate of 0.1 mV/s.](image)

Fig. 4.4. Cyclic voltammograms of VXC in 1 M LiPF₆ at a sweep rate of 0.1 mV/s.
Fig. 4.5 Cyclic voltammograms of graphite at a sweep rate of 0.1mV/s.
4.4 Sugar Carbon Materials as Anode for Lithium-ion Batteries

4.4.1 X-ray Diffraction

Fig. 4.6 shows the X-ray patterns of sugar carbons prepared at the different temperatures. Two peaks, marked as (002) and (100), are observable for all those sugar samples treated at different temperatures, while a small broad (110) peak can be seen only for the sample treated at 1000 °C. These peaks indicate that the stacking order of graphite planes of the sugar carbons are at random. Although intensity of diffraction peaks (002), (100) and (110) increased a little with increasing heat-treatment temperature (HTT), the crystallinity of the sugar carbons was low and does not change significantly in the HTT range between 700 and 1000 °C. However, the discharge/charge curves are significantly affected by HTT as shown in follows.

4.4.2 Charge/Discharge Test

Fig. 4.7 Shows the discharge/charge curves of the sugar carbons during the first two cycles. The results from the four samples are summarised in table 4.3. As the temperature of pyrolysis (T_p) is increased from 700 to 1000°C, the charge capacities of the sugar carbons increase (from 192 to 372 mAh/g). In all the sugar carbons the cycle efficiencies (Q_ch/Q_dis) of the first cycle are very low and the cycle efficiencies of the second cycle are all above 85%. This can be explained by that the major part of the current during the first cycle may have been consumed by some irreversible reactions such as the formation of the passivating film on the electrode surface due to the decomposition of the electrolyte, etc [103].
The sugar carbon tested in this study shows a large irreversible capacity. The irreversible capacities decrease from 282 to 156mAh/g as T_p is increased. This trend is similar to that observed in the recent work of Xing et al [106].

Table 4.3  Heat treatment temperature (HTT) and the charge/discharge capacity

<table>
<thead>
<tr>
<th>Sample</th>
<th>HTT (°C)</th>
<th>Discharge Capacity (mAh/g)</th>
<th>Charge Capacity (mAh/g)</th>
<th>Irreversible Capacity (mAh/g)</th>
<th>Cycle efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1st</td>
<td>2nd</td>
<td>1st</td>
<td>2nd</td>
</tr>
<tr>
<td>A</td>
<td>700</td>
<td>474</td>
<td>211</td>
<td>192</td>
<td>182</td>
</tr>
<tr>
<td>B</td>
<td>800</td>
<td>415</td>
<td>188</td>
<td>161</td>
<td>155</td>
</tr>
<tr>
<td>C</td>
<td>900</td>
<td>470</td>
<td>257</td>
<td>249</td>
<td>221</td>
</tr>
<tr>
<td>D</td>
<td>1000</td>
<td>529</td>
<td>278</td>
<td>372</td>
<td>241</td>
</tr>
</tbody>
</table>
Fig. 4.6. XRD patterns of sugar carbons pyrolyzed at different temperatures.
Fig. 4. Charge/discharge behavior of sugar carbon prepared at different treatment temperatures at a current density 0.125 mA/cm². (a) 700 °C, (b) 800 °C, (c) 900 °C and (d) 1000 °C
4.5 The Effect of the Pre-lithiation Treatment on Sugar Carbons

4.5.1 The pre-lithiation Process

In order to investigate the pre-lithiation process and to optimize the pyrolyzing temperature ($T_{pyr}$) on the electrochemical properties of pyrolyzed sugar carbon electrode or on the sugar precursors, different pyrolyzing temperatures, from 500 °C to 1100 °C have been chosen and tested.

After pyrolysis of the sugar precursors at different $T_{pyr}$, the sugar carbon was well ground and mixed with LiCO$_3$ in a mole ratio of 1:6 (Li:C). The pre-lithiation treatment was carried out on a well mixed sugar carbon lithium salt powder in a tube furnace at 800 °C for 12 hours under constant argon flow.

4.5.2. X-ray Diffraction of the Pre-lithiated Sugar Carbons

Powder XRD measurements were performed on the sugar carbons after the pre-lithiation treatments. Comparing the pre-lithiated sugar carbons with those without the pre-lithiation treatment shown in Fig. 4.8, the diffraction patterns of those samples are similar. All of these powders are disordered carbons. However, the Bragg peak (002) of the pre-lithiated samples shows a slightly shift to the left. These results suggest that the pre-lithiation treatment may have modified the interlayer distance spacing of 002 planes ($d_{002}$).

As calculated by the software, Trance 3.0, the $d_{002}$ shift from 4.03 ~ 4.10 to 3.93 ~ 4.0 Å, however, these results were based on a rough calculation since the exactly peak values from these diffraction diagrams were hard to determine.
Fig. 4.8 Powder XRD diagrams of pre-lithiation treated and without treated sugar carbon.
4.5.3 SEM Analysis of the Pre-lithiated Sugar Carbons

Scanning electron microscopy (SEM) was performed on both non-treated and the pre-lithiated sugar carbons and the SEM results are presented in Fig. 4.9. Differences in the crystal morphology and size of the sugar carbon with and without the pre-lithiation treatment can be distinguished from these SEM observations. The non-treated samples show sharp crystal edges and comparatively larger crystal sizes while the pre-lithiation treated samples show modified, non-sharp crystal edges and comparatively small crystal sizes. These were attributed to the strong oxidation occurred in the prelithation process. These changes in the surface morphology and microstructure of the carbon particles after the treatment are thought to affect the electrochemical properties of the electrode, and these effects were investigated by electrochemical methods.

4.5.4 Electrochemical Experiments on the Pre-lithiated Sugar Carbons

Charge/discharge tests and cyclic voltammetry (CV) were performed to tell the effect of the pre-lithiation treatment on the reversible capacities and electrochemical properties of the sugar carbon anodes. Fig. 4.10 shows the charge/discharge curves and the data are listed in table 4.4.
Fig. 4.9. SEM of Non-treated (a) and treated sugar carbon (b) (1000°C).
Fig. 4.10. First and second charge/discharge curves of the pre-lithiated sugar carbon and the non-treated carbon (Tpyr = 1000 °C) at a current density 0.125mA/cm².
The results indicated that the pre-lithiated treated hard carbon showed a reduction in irreversible capacity of about 23mAh/g and both the (first) charge and discharge capacity were increased.

Table 4.4 Results of the irreversible capacities of the –prelithium treated and non-treated sugar carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>First discharge capacity (mAh/g)</th>
<th>First charge capacity (mAh/g)</th>
<th>Irreversible capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated carbon</td>
<td>550</td>
<td>416</td>
<td>134</td>
</tr>
<tr>
<td>Non-treated carbon</td>
<td>529</td>
<td>372</td>
<td>157</td>
</tr>
</tbody>
</table>

Figs. 4.11 and 4.12 show the results of the CV measurements. The peak currents for the treated carbon are higher than those of the non-treated carbon, which is in agreement with the observed enhanced discharge capacity.
Fig. 4.11 Cyclic voltammograms of non-treated sugar carbon

\( T_{pyr} = 1000 \, ^\circ C \) at a sweep rate of 0.1 mV/s.
Fig. 4.12 Cyclic voltammograms of the pre-lithiated sugar carbon 
\( (T_{pyr}=1000 \, ^\circ C) \) at a sweep rate of 0.1mV/s.
4.6 Summary

(1) Several synthesized and commercially available carbonaceous materials have been investigated as anodes for lithium-ion battery. Among those tested materials, graphite shows the highest galvanostatic capacity and the lowest irreversible capacity. The glass carbon (GC) shows poor capacity, but its cycling behavior is the best.

(2) Sugar carbons were synthesized and investigated. The capacities of the sugar carbons increased as the pyrolysis temperature ($T_p$) increased.

(3) The pre-lithiation treatment was used for the sugar carbons. After treatment, the surface morphology of the samples has been modified, the particle size was reduced and made more uniform. The irreversible capacity was reduced. It is thought that further improvement could result from optimisation of the pre-lithiation process and further experiments are required for exploration the pre-lithiation mechanism. However, it is beyond of this study.
Chapter 5.

An Anode Material with Perovskite Structure for Rechargeable Li-Ion Batteries

5.1 Introduction

Conventional anodes used in rechargeable lithium-ion batteries use various kinds of carbon-based materials [107-100]. Lithium ions are stored reversibly between a layered carbon framework, which thereby developed an electrochemical potential significantly negative to the cathode. The maximum theoretical capacity of graphite (LiC$_6$) is 372 mAh/g and its volumetric capacity is 800 mAh/ml [111]. Exceeding the stoichiometric limit of LiC$_6$ increases the Li-storage capacity of carbon materials. However, this often leads to the formation of hazardous metallic Li dendrites on the electrode surface [112]. Although carbon-based anodes provide reasonable behaviour in commercial cells, there are certain limitations, such as the first cycle passivation of the carbon negative electrode which consumes positive-electrode lithium and results in a comparatively low volumetric capacity due to the low density of the carbon material [113]. Sometimes, volumetric energy density of a battery (Wh/L) becomes more important than gravimetric energy density (Wh/kg), especially when the cell volume is strictly limited as the case of small-size batteries required.
Chapter 5 An Anode Material with Perovskite Structure for Rechargeable Li-Ion Batteries

The perovskite-type oxides of $\text{ABO}_3$ present various interesting functions such as ferroelectricity, ion conductivity, magnetism, catalysis and super conductivity. Recent reports show that the perovskite-type oxides containing the rare earth metals exhibit very high lithium ionic conductivity at room temperature, when they were used as cathodes for rechargeable lithium-ion batteries. It has been suggested that inserted lithium ions could occupy A-site vacancies then 3c–sites of $\text{ABO}_3$ oxide and the Lithium insertion leads to the reduction of transition metal (B cation) in electroneutrality [114]. In the present study, a $\text{ABO}_3$ perovskite-type oxide, barium metaplumbate ($\text{BaPbO}_3$), was synthesized and investigated as a possible anode for the lithium-ion battery. The possible mechanism of lithium-ion intercalation into and de-intercalation from the oxides was also proposed. $\text{BaPbO}_3$ is a conductive ceramic at room temperature and also a superconductor at low temperature. The crystal structure of $\text{BaPbO}_3$ is an orthorhombic perovskite type. In the $\text{BaPbO}_3$ oxide, Pb ion (B cation) occupies the centre of an octahedron which consist of six oxygen ions while the valence of Pb ion is usually fixed at four. It would be very interesting and meaningful if $\text{Pb}^{4+}$ can be reduced by the insertion of Li, such as suggested in the situation of $\text{ABO}_3$ oxides containing rare earth metals. Since different oxygen contents of the oxide (oxygen deficient forms of $\text{BaPbO}_3$ compounds) can be formed, which will result in different conductivities, structure and electrochemical behaviour. To clarify this, single phase $\text{BaPbO}_3$ and two phases of $\text{BaPbO}_3$ ($\text{PbO})_x$ were investigated and the results were compared in this study.
5.2 Experimental

BaPbO₃ was synthesised through a solid-state reaction method using BaCO₃, and Pb₃O₄ (SIGMA products) with different ratios as starting materials [121]. In order to obtain a homogeneous product, these raw materials were mixed and wet-milled in a ball mill for 4 hours. The mixture was dried, ground and pressed into pellets 25 mm in diameter and 2 mm thick at a pressure of 750 kg/cm². The pellets were placed into a sealed tube furnace with a program controller and fired at 600°C for 4 hr and 1000 °C for 1.5 hr in oxygen. An optimum control program for preparing the sample was chosen after several trials and thermal analyses of the samples. The solid-state reaction in air or O₂ can be expressed by:

\[
6 \text{BaCO}_3 + 3 \text{Pb}_3\text{O}_4 + \frac{3}{2} 0_2 = 6 \text{BaPbO}_3 + 3 \text{PbO} + 6 \text{CO}_2 \quad (5-1)
\]

Normally, a two phase compound of BaPbO₃ and PbO will be obtained by the process while a single-phase of BaPbO₃ can be obtained by extending the high temperature sintering to get rid of unreacted PbO.

Electrochemical experiments are performed in coin-type test cells with an electrolyte of 1M LiPF₆ dissolved in a 30/70 v/v mixture of EC/DEC solution, and the separator was a microporous film (Celgard 2500). The BaPbO₃ pellets obtained were ground and/or ball milled into fine powder. The powder was used either without any additives or mixed with 10 wt.% graphite powder (1-2 μ, Aldrich Chem Co. Inc.) and 5% PVDF binder dissolved in dimethyl phosphate to form a thin film or a pellet electrode for lithium test cells. Test cells were assembled in an argon-filled glove box. These cells were discharged first from their open circuit voltages (OCV) at a constant current of 0.5 mA/cm² and then cycled between 0 and 1.70 V. Cyclic voltammograms were performed on three electrode test cells, Li foil used as both the counter and the reference
electrodes at a scanning rate of 0.1 mV s\(^{-1}\).

### 5.3 Results and Discussion

Fig. 5.1 shows a schematic illustration of the perovskite structure of BaPbO\(_3\) and Table 5.1 presents the cell constants and other physical properties [121]. A single-phase of BaPbO\(_3\) was obtained by extending the high temperature sintering to get rid of remixed PbO.

Thermogravimetric and differential thermal analysis (TG/DTA) measurements were carried on the mixture of BaCO\(_3\) and Pb\(_3\)O\(_4\) powder at a heating rate of 200 \(^{\circ}\)C/h with a standard sample of \(\alpha\)-Al\(_2\)O\(_3\) and the results were shown in Fig. 5.2.

Pb\(_3\)O\(_4\) decomposes into PbO and O\(_2\) above 540 \(^{\circ}\)C, as expected from equation (5-1), promotes the formation of BaPbO\(_3\). The large endothermic peak in the DTA curve at 850 \(^{\circ}\)C in Fig. 5.2 is due to the melting and evaporation of unreacted PbO.

X-ray diffraction patterns of a single-phase of BaPbO\(_3\), two phases BaPbO\(_3\)/PbO and the pure PbO are shown in Fig. 5.3. After charge/discharge cycling tests, each test cell was disassembled and the electrode was ground and analyzed by XRD again. Fig. 5.3 shows that the PbO phase in the two phase patterns of BaPbO\(_3\)/PbO electrode disappeared after cycling, which indicated that PbO may react with Li and to form a new compound or a Pb-Li alloy. After the cycling test, no distinguishable lattice parameter change in the single phase of BaPbO\(_3\) was observed, which indicates the perovskite-structure of BaPbO\(_3\) is stable.
Table 5.1

<table>
<thead>
<tr>
<th>BaPbO₃ (T &gt; 400 °C)</th>
<th>$a₀$ (Å)</th>
<th>$b₀$ (Å)</th>
<th>$c₀$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray density</td>
<td></td>
<td></td>
<td>8.40 (g cm³)</td>
</tr>
<tr>
<td>Electric resistivity</td>
<td></td>
<td></td>
<td>$8.3 \times 10^{-4}$ (Ω·cm, at 25 °C)</td>
</tr>
</tbody>
</table>

Fig. 5.1 Schematic illustration of the perovskite structure of BaPbO₃:

- A-site: Ba²⁺;
- B-site: Pb⁴⁺, O⁻ - O.

98
Fig. 5.2 DTA/TGA of the mixture of BaCO$_3$ and Pb$_3$O$_4$ in O$_2$

at the heating rate of 200 °C/h.
Fig. 5.3. X-ray diffraction pattern for pure $\text{BaPbO}_3$, $\text{BaPbO}_3(\text{PbO})_x$, and pure $\text{PbO}$ before and after cycling tests.
Fig. 5.4 Cyclic voltammograms of the BaPbO$_3$ electrode in a three-electrode test cell, the previously five cycles at a scanning rate of 0.1 mV/s.

Fig. 5.4 shows cyclic voltammograms (CV) of the pure phase BaPbO$_3$ electrode. The CV experiment started at the open-circuit voltage of the test cell and then scanned to 0 V, at a scanning rate of 0.1 mVs$^{-1}$. An oxidation peak appears at about 0.55 V with good cycleability. The CV curves of Fig. 5.4 approach a steady shape after about 5 cycles, therefore, it is considered that the intercalation and de-intercalation of lithium
cycles, therefore, it is considered that the intercalation and de-intercalation of lithium ions are reversible for the pure BaPbO$_3$ and these reactions occur in the voltage range from 0.01 to 0.7 V versus Li/Li$^+$ at a scanning rate of 0.1 mV/s. The oxidation/reduction peaks suggest the possibility of the intercalation/de-intercalation of lithium ions could occur in the pure BaPbO$_3$ electrode. However, the intercalated lithium ions occupy which positions in the lattice of BaPbO$_3$ and if Pb$^{4+}$ is reduced by the insertion of Li or not are still unknown. Further work is required to clarify this but that is beyond of this study.

Fig. 5.5 Cyclic voltammograms of the BaPbO$_3$(PbO)$_x$ electrode in a three-electrode test cell, the previously five cycles at a scanning rate of 0.1 mV/s.
Fig. 5.5 shows CVs of the BaPbO$_3$(PbO)$_x$ electrode (two phase compound of BaPbO$_3$(PbO)$_x$. Two distinguishable reduction peaks at 1.43 and 1.15 V were observed, respectively, in the first discharge curve for the two phase compound electrode. These two reduction peaks were attributed to the reduction of remained PbO in the compound, i.e., Pb$^{2+}$ → Pb$^+$ and Pb$^+$ → Pb, respectively. After the first discharge-charge cycle, the cut-off voltages were set at 0.01 and 1.70 V. The following cycles show two distinct oxidation peaks, marked $a$ and $b$, located at about 0.5 V and 0.7 V, respectively.

The two oxidation peaks reach the maximum values at the second cycle and then declined with cycling. It is noticeable that the peak voltage values are shifted to the left a little with cycling, which implies a poor cycleability of the compound electrode. This may be explained by that the remained PbO in the BaPbO$_3$(PbO)$_x$ compound could react with Li during the electrochemical intercalation/de-intercalation to form a new compound, possibly a Pb-Li alloy via a reaction of

$$\text{PbO + 6.4 Li} \rightarrow \text{Li}_{4.4}\text{Pb} + \text{Li}_2\text{O} \quad (5-2)$$

This is an irreversible reaction, which consumes both PbO and Li. This is in consistent with the X-ray patten of Fig. 5.3 in which PbO peaks disappeared after several tenths cycling.

In order to clarify that the cathodic and anodic peaks of Fig. 5.5 are from the reaction of PbO with Li, assumed by the equation (5-2). A pure PbO electrode was used to substitute for the two phase BaPbO$_3$(PbO)$_x$ electrode in the same three electrode system. A CV plot of the pure PbO was given in Fig. 5.6, which shown a similar pattern with
supports the suggestion of the formation of new compound between PbO and Li. This reaction is also distinguishable to that of the pure BaPbO$_3$ system shown in Fig. 5.3.

Fig. 5.7 shows the discharge capacity versus the cycle number of pure BaPbO$_3$ and the BaPbO$_3$(PbO)$_x$, respectively. The first irreversible discharge capacities of two electrodes show different value. The irreversible discharge capacity of the pure BaPbO$_3$ electrode is noticeably decreased. This result indicates that the pure phase BaPbO$_3$ not only enhances the electronic conductivity but also presents a good cyleability.

![Cyclic voltammogram of the PbO electrode in a three-electrode test cell, at a scanning rate of 0.1 mV/s.](image)

Fig. 5.6 Cyclic voltammogram of the PbO electrode in a three-electrode test cell, at a scanning rate of 0.1 mV/s.
Fig. 5.7 Cycle dependence of discharge capacity of the BaPbO$_3$ and BaPbO$_3$(PbO)$_x$ at a current density of 0.5 mA/cm$^2$. 

**Diagram**: 
- ▲ BaPbO(PbO)$_x$ (0<$x$<1) 
- • BaPbO$_3$ 

**Axes**: 
- **Y-axis**: CAPACITY (mAh/g) 
- **X-axis**: CYCLE NUMBER 

**Legend**: 
- ▲ BaPbO(PbO)$_x$ (0<$x$<1) 
- • BaPbO$_3$ 

**Text**: 
- Chapter 5 An Anode Material with Perovskite Structure for Rechargeable Li-Ion Batteries
Lithium ions could be electrochemically intercalated in and de-intercalated from perovskite-type oxide BaPbO$_3$. These intercalation and de-intercalation reactions occur at the voltage range from 0 to 0.7 V versus Li/Li$^+$. The study results show that the pure phase material presents a good cycleability when tested as an anode in the Li-ion battery. The gravimetric capacity of the BaPbO$_3$ is in the order of 110 mAh/g and a volume capacity of 960 mAh/cm$^3$. Since this material has high inherent electronic conductivity and a good cycleability, it could be used as an anode without any conductive additives. However, non-pure phase BaPbO$_3$ oxides, such as BaPbO$_3$(PbO)$_x$ compound presents a different reaction mechanism in a Li-ion test cell. Further study in this system is required for exploring the intercalation and de-intercalation mechanism.
6.1 Review of the Study

A thorough literature review has been given at the beginning of this study with emphasis on the anodes of lithium-ion batteries. Materials and chemicals, either chosen from commercially available products or prepared in this study, have been described in detail in the Chapter 2. Experimental techniques and methods applied in this study are also included in this chapter.

Based on the aims of this study, the major research performed can be divided into the following three subjects:

(1) Synthesis and study of tin-based oxide composites as an anode for lithium-ion batteries.

(2) Synthesis and study of the carbonaceous materials as anodes for lithium-ion batteries and study of the influences of the pyrolysis temperature and the pre-lithiation treatment on the cell performance.

(3) Synthesis and investigation of the conductive ceramic, BaPbO$_3$, as an anode for lithium-ion batteries.
6.2 General Conclusions

The major study results from the above three aspects have been summarised in Chapters 3, 4 and 5, respectively. General conclusions can be drawn from these summaries and are presented below:

1. Tin oxide composites represent a new class of anode material for the anode of Li-ion cells. Stannic oxide shows the highest capacity. \( \text{SnO}_2 \) prepared by the sol-gel method presents a higher capacity than that of \( \text{SnO}_2 \) obtained from commercially available products, due to a finer particle size, more homogeneous particle size distribution and therefore a higher specific surface area can be obtained through the sol-gel method.

The capacity retention of the tin-based anode can be improved when the voltage cut-off is selected appropriately. A better cycling life was obtained at the voltage range between 0.3-1.0V for the \( \text{SnO}_2 \) anode.

2. Carbonaceous materials have been synthesised. Among those materials tested, the graphite presents the highest capacity and but a poor cyclic durability, while the glass carbon (GC) shows good cycling behaviour.

Sugar carbon was synthesized. The capacities of the sugar carbon is increased as the pyrolysis temperature is increased from 700 to 1000 °C.

The pre-lithiation treatment method can reduce the irreversible capacity of the sugar carbon. After the treatment, the surface morphology of the samples is modified and a more uniformed particle size distribution is obtained.

3. Lithium ions could be electrochemically intercalated in and de-intercalated from the perovskite-type oxide \( \text{BaPbO}_3 \). These intercalation and de-intercalation
reactions occurred at the voltage range from 0 to 1.7 V versus Li/Li\(^+\), which suggests that this material could be one of the candidates for the anode in lithium ion batteries. The gravimetric capacity of the BaPbO\(_3\) electrode is about 110 mAh/g and the volume capacity is about 960 mAh/cm\(^3\). Since this material presents a high inherent electronic conductivity, it can be used as electrode material without any conductive additives. However, experimental results show that a two phase compound of (BaPbO\(_3\) and PbO) electrode is detrimental to the cell cycling performance. A possible reason for the sharp decline of the cycling capacity of this electrode may be explained by a reaction between the lithium and PbO, as observed when using a pure PbO as an anode during the experiment.
References


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References


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