Phase Transformations and Microstructural Design of
Lithiated Metal Anodes for Lithium-ion
Rechargeable Batteries

by

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Submitted to the Department of Materials Science and Engineering
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ABSTRACT

There has been great recent interest in lithium storage at the anode of Li-ion rechargeable battery by alloying with metals such as Al, Sn, and Sb, or metalloids such as Si, as an alternative to the intercalation of graphite. This is due to the intrinsically high gravimetric and volumetric energy densities of this type of anodes (can be over an order of magnitude of that of graphite). However, the Achilles’ heel of these Li-Me alloys has been the poor cyclability, attributed to mechanical failure resulting from the large volume changes accompanying alloying. Me-oxides, explored as candidates for anode materials because of their higher cyclability relative to pure Me, suffer from the problem of first cycle irreversibility. In both these types of systems, much experimental and empirical data have been provided in the literature on a largely comparative basis (i.e. investigations comparing the anode behavior of some new material with older candidates). It is the belief of the author that, in order to successfully proceed with the development of better anode materials, and the subsequent design and production of batteries with better intrinsic energy densities, a fundamental understanding of the relationship between the science and engineering of anode materials must be achieved, via a systematic and quantitative investigation of a variety of materials under a number of experimental conditions.

In this thesis, the effects of composition and processing on microstructure and subsequent electrochemical behavior of anodes for Li-ion rechargeable batteries were investigated, using a number of approaches. First, partial reduction of mixed oxides including Sb-V-O, Sb-Mn-O, Ag-V-O, Ag-Mn-O and Sn-Ti-O, was explored as a method to produce anode materials with high cyclability relative to pure metal anodes, and decreased first cycle irreversibility relative to previously produced metal-oxides. The highest cyclability was achieved with anode materials where the more noble metal of the mixed oxide was reduced internally, producing nanoscale active particles which were passivated by an inactive matrix.

Second, a systematic study of various metal anode materials, including Si, Sn, Al, Sb and Ag, of different starting particle sizes was undertaken, in order to better understand the micromechanical mechanisms leading to poor cyclability in these pure metals. SEM of
these materials revealed fracture in particles of > 1 μm after a single discharge/charge cycle, consistent with literature models which predict such fracture due to volumetric strains upon lithiation. However, TEM of these materials revealed a nanocrystalline structure after one cycle that in some metals was mixed with an amorphous phase. STEM of anode materials after 50 cycles revealed a dissociation of this nanostructure into nanoparticles, suggesting a failure mechanism other than volumetric strains, such as chemical attack.

Finally, the appearance of the amorphous phase was investigated in lithiated Si, Sn, Ag and Al metal anode systems. A new mechanism, *electrochemically-induced solid-state amorphization* was proposed and explored via experiments using calibrated XRD and TEM. Experimental observations of these various Me systems subjected to different degrees of lithiation supported such phenomenon. Microstructural data from XRD and HREM of the Li-Si model system in conjunction with the electrochemical data provided strong evidence that formation of a non-crystalline metal stable phase and suppression of the equilibrium crystalline phases could occur in lithiated metal alloys. A thermodynamic and kinetic rationale for such solid-state amorphization was presented along with supporting experimental data on a conventional solid-state bilayer thin film. The amorphous material was hypothesized to act as a medium for subsequent nucleation and growth of nanocrystallites, and as a preferential site for chemical attack leading to anode disintegration upon further cycling.

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Chapter 1

Introduction and Background

1.1 Lithium-ion Rechargeable Battery

The increased demand for efficient power sources, the desire to decrease oil consumption and the hope of having a cleaner environment have prompted worldwide research in high energy density rechargeable batteries. Compared to earlier developed rechargeable battery systems such as lead-acid, nickel-cadmium (NiCd), or nickel-metal hydride (NiMH) batteries, lithium-ion (Li-ion) batteries have shown a much higher energy density on a weight and volume basis (Fig 1.1), which makes them more attractive for current high energy consumption applications such as laptop computers, cellular phones, and personal digital appliances (PDAs). If the cost of Li-ion technology can be substantially reduced and reliability increased, it is likely to be used in larger-scale applications such as backup power and hybrid or fully-electric vehicles.

Research on primary (disposable) lithium batteries began in the late 1950’s, and in 1973, commercial primary lithium batteries were introduced. The first rechargeable lithium battery to be commercialized used MoS$_2$ as the intercalation cathode, and lithium metal as the anode. This battery proved to be unsafe due to lithium dendrite formation during cycling. In 1991, Sony put a “Li-ion” rechargeable battery on the market for the first time. While of course all lithium based batteries transport lithium ions, in the
battery field the term “Li-ion” has come to mean the use of an intercalation cathode with an anode in which the chemical potential of lithium remains below that of metallic lithium in normal use, so that lithium metal dendrites do not form. This type of battery is also known as a “rocking-chair” battery.

A Li-ion battery consists of three basic working parts: an anode (negative electrode), a cathode (positive electrode) and a Li-ion conducting electrolyte. The operating principle is the difference in the chemical potential of \( \text{Li}^+ \), \( \mu_{\text{Li}} \), between the anode and the cathode. A schematic picture of the system is shown in Fig. 1.2.\(^4\) The anode and the cathode accommodate \( \text{Li}^+ \) ions at higher and lower potential, respectively.

At each electrode, lithium ions have an electrochemical potential given by:

\[
\eta_{\text{Li}}^I = \mu_{\text{Li}}^I + ze\phi^I \quad (1.1)
\]

where \( \eta_{\text{Li}}^I \) = electrochemical potential of Li at electrode I

\( \mu_{\text{Li}}^I \) = chemical potential of \( \text{Li}^+ \) at electrode I

\( z \) = charge of the species

\( e \) = elementary charge = \( 1.60219 \times 10^{-19} \) C

\( \phi \) = electric potential at electrode I

At equilibrium, the electrochemical potential is equilibrated between cathode and anode, giving an open-circuit voltage for the battery, \( \Delta \Phi \), of

\[
\Delta \Phi = \frac{\left| \mu_{\text{Li}}^{\text{cathode}} - \mu_{\text{Li}}^{\text{anode}} \right|}{F} \quad (1.2)
\]

where \( \Delta \Phi \) = Voltage of a battery

\( \mu_{\text{Li}}^{\text{cathode}} \) = chemical potential of \( \text{Li}^+ \) at the cathode
\( \mu_{\text{Li}^+}^{\text{anode}} \) = chemical potential of Li\(^+\) at the anode

\( F \) = Faraday constant = 96,485 C/mole

The electrolyte acts as an ionic conductor and electronic insulator between the two electrodes, through which the Li\(^+\) ions flow. During the discharging process, lithium ions in the anode (with higher \( \mu_{\text{Li}} \)) exit the electrode and migrate across the electrolyte to the cathode side of the battery (with lower \( \mu_{\text{Li}} \)). The positive charges of Li\(^+\) ions are balanced by negatively charged electrons (\( e^- \)) traveling through an external circuit. This external current produces power when it encounters resistance.

During the charging process, electrons and Li\(^+\) ions travel from the cathode back to the anode. This time, however, an external voltage is applied in order to overcome the chemical potential difference that drove the discharge process.

A schematic diagram of a typical Li-ion battery, along with the commonly used components, is shown in Fig 1.3\(^4\). When a lithiated cathode such as LiCoO\(_2\) is used with an unlithiated anode such as carbon or one of the metals discussed in this thesis, the battery is assembled in the discharged state. When a lithiated anode such as metallic lithium or LiAl is used with an unlithiated cathode, such as V\(_2\)O\(_5\), the battery is assembled in the charged state. Most commercial Li-ion batteries are of the former type.

1.2 Basic Properties of Rechargeable Batteries

1.2.1 Voltage

The equilibrium or open-circuit battery voltage, \( V \), has an intrinsic thermodynamic value for a specific system (Eq. 1.2), and varies throughout the charge-discharge process with the lithium concentration in the anode and cathode. However, this
value may deviate from the equilibrium value due to internal polarization under load. The internal resistance of the battery results in an ohmic drop, and the accumulation of ionic species at interfaces results in concentration polarization. As it is preferable to have a predictable battery voltage during use, this deviation from the ideal voltage should be minimized. Batteries with low internal resistance and high \( \text{Li}^+ \) diffusivity are generally desirable.

1.2.2 Capacity

Capacity \( (Q) \) of a battery is the amount of charge it can hold, generally given in units of milliamp-hours (mAh). A Li-ion rechargeable battery marketed now, for example, Sony US18650 (diameter 18 mm, height 65 mm and weight 45 g) has a capacity of 1800 mAh.\(^4\) For comparison purposes between different types of batteries or between different materials, \( Q \) is usually expressed in units of mAh/g (gravimetric capacity) or mAh/cm\(^3\) (volumetric capacity). The theoretical capacity of a storage material can be calculated from the number of Li\(^+\) ions an electrode can accept or release per weight of the active material:

\[
Q_T = \frac{n}{MW} \cdot F \cdot t
\]  

(1.3)

where 
- \( Q_T \) = theoretical capacity (mAh/g)
- \( n \) = number of moles of Li/ moles of active material
- \( MW \) = molecular weight of the active material (g/mole)
- \( F \) = Faraday Constant
- \( t \) = time (hours)
Most Li-ion batteries are constructed to have a slight excess capacity in the anode storage material (about 10%) so that lithium metal plating does not occur. This condition is termed "cathode limited." The total capacity of the battery (in mAh) is then equal to the cathode capacity, although on a gravimetric or volumetric basis, all of the constituents must be accounted for. Experimentally, if the current and mass of the active material in a cell is known, the capacity of the active material is simply calculated from:

$$Q = I \cdot t$$  \hspace{1cm} (1.4)

where $Q = \text{capacity (mAh/g)}$

$I = \text{current rate (mA/g)}$

$t = \text{time (hour)}$

Two kinds of irreversibility are important in rechargeable batteries. The first-cycle irreversibility is the difference between first-charge and first-discharge capacity (for a lithiated cathode), arising when lithium is trapped in the anode or is consumed irreversibly in a side reaction during the first cycle. In later cycles, the coulombic efficiency, defined as $Q_{\text{discharge}}/Q_{\text{charge}}$, is the difference in total current consumed during charge and discharge processes. This can also be less than unity due to side reactions or lithium trapping. Typical first-cycle irreversibility in commercial batteries is 5%, and typical coulombic efficiency is greater than about 99.5%, leading to an effectively complete capacity loss after approximately 500 cycles.
1.2.3 Energy Density

Energy density of a battery, $E$, is defined as the amount of energy a battery can deliver per unit weight or volume (Wh/g, Wh/kg or Wh/cm³, Wh/liter) at a certain current rate.

$$E = Q \cdot V$$  \hspace{1cm} (1.5)

where $Q$ = Capacity (Ah/kg, Ah/liter)

$V$ = Battery voltage (V)

1.2.4 Power Density

Power of a battery describes how much energy a battery can deliver per unit time. The common unit of power density is W/kg or W/liter. Power density of a battery can be calculated from:

$$P = I \cdot V$$  \hspace{1cm} (1.5)

where $P$ = Power density (W/kg)

$I$ = Current density (A/kg)

$V$ = Battery voltage (V)

It is desirable to have a battery with high power density as well as high energy density. However, as illustrated in by a Ragone plot (Fig 1.4), which is a plot of energy density vs. power density of a battery, as the power density of a battery increases, the energy density usually drops. This trade-off is due to the limiting transport properties of Li⁺ through the system. At high power, a current is drawn from one electrode at a high rate. If the rate is high enough that Li⁺ ions cannot diffuse fast enough out of one electrode to the other electrode, not all of the Li⁺ can be extracted from the electrode. This gives rise-
to sub-optimum capacity leading to decrease in energy density as the power density is increased.

1.2.5 Cyclability

A battery with high cyclability is necessary; it must be able to withstand a large number of charge/discharge cycles with little or no capacity drop. Laptop manufactures, for example, typically demand batteries with < 20-40% initial capacity depreciation over 300-500 cycles at room temperature. For use in electric vehicles, a cyclability of >500 cycles is expected.

1.3 Rechargeable Lithium Battery Anodes

The following lists desirable properties of anode materials

- Ability to accommodate a high number of Li\(^+\) ion per unit weight or volume of the anode (for high capacity and high energy density)
- Low voltage with respect to lithium (for high energy density and power density)
- Good electronic conductivity (to minimized polarization. Moreover, less amount of conductive additives will be necessary which leads to less dead weight in the battery)
- High Li\(^+\) ion diffusivity (If Li\(^+\) can diffuse in and out fast, the current can be charged/drawn to/from the electrode at a high rate leading to high power density.
  High Li\(^+\) ion diffusion also leads to low polarization (that is caused by charge accumulation at the surface of the electrode.))
- Good cyclability
- Compatibility with the electrolyte system
- Ease of processing
- Long storage life
- Wide operating temperature range
- Compliance with environmental concerns
- Low cost

Numerous types of materials have been explored as anodes for Li rechargeable batteries. The following sections give examples of different types of currently known anodes along with their advantages and drawbacks.

1.3.1 Lithium Metal

For an anode, lithium metal seems to be an obvious choice because of its high specific capacity (3860 mAh/g, 2061 mAh/cm³) and high reduction potential (giving a high voltage battery). Lithium metal has commercially been used as the negative electrode in primary batteries. However, it was found to be inappropriate for rechargeable batteries because of safety problems due to overheating, and its poor cyclability due to corrosion and dendrite growth. The use of non-aqueous electrolytes promotes the formation of a passivating layer at the interface between the metal and electrolyte, which prevents further corrosion. However this passivating layer is often not uniform, creating a chemical perturbation at the surface of the metal that aids dendrite growth and thus leads to short circuiting of the batteries. Materials in the following section have been developed in an attempt to resolve this problem.
1.3.2 Carbon

Following safety problems of lithium metal negative electrodes, attention turned to replacing lithium by an anode materials with a significantly lower standard reduction potential than that of the positive electrode.\textsuperscript{12} Since the first commercialized Li-ion rechargeable battery, carbon, which is capable of accepting and exchanging Li per 6 C with low price, has been used as the negative electrode.\textsuperscript{13} While it can accept and release Li\textsuperscript{+} reversibly for $>500$ cycles with low voltage relative to Li metal ($\sim$0.1V), carbon has the disadvantages of having low gravimetric and volumetric capacity, only 372 mAh/g (ten times lower than lithium metal) and 837 mAh/cm\textsuperscript{3} respectively.\textsuperscript{9}

1.3.3 Other Intercalation compounds

Other types of insertion electrodes have also been explored as alternatives to lithium metal. These include transition metal oxides (i.e. WO\textsubscript{2}, MoO\textsubscript{2})\textsuperscript{14}, transition metal sulfides (i.e. TiS\textsubscript{2})\textsuperscript{15}, and other intercalation hosts such as Cu\textsubscript{2}Sb\textsuperscript{16}, Cu\textsubscript{6}Sn\textsuperscript{17} and InSb\textsuperscript{18}. Although it has been shown that these types of intercalation compounds can have a reasonable cycling life, they typically exhibit capacities lower than that of carbon at a much higher voltage relative to Li metal, giving rise to a lower voltage battery.

1.3.4 Lithiated Metal Anodes

Because of many problems associated with the use of lithium metal as an anode, researchers have also considered Li-metal alloys as an alternative. Several systems of Li-metal alloys, Li\textsubscript{x}Me (Al, Bi, Sn, Sb, In,...), with fast diffusion coefficient of Li\textsuperscript{+} have been studied.\textsuperscript{19-32} These alloys can exhibit high capacity with relatively low voltage with
respect to Li metal. However, disintegration of electrodes upon lithiation and delithiation leading to poor cyclability has prohibited them from being used commercially.\textsuperscript{7} Recently, Idota, et. al \textsuperscript{33} of Fuji Celltec Co. Ltd. suggested that metals in the oxide form could be cycled reversibly. The reversible capacity of the new materials could be as high as 600 mAh/g. Since this discovery, many research groups have developed an interest in metal oxide based anodes, especially tin based oxide anodes.\textsuperscript{34-40} However, from their studies, it was found that a major limiting factor was a large irreversible capacity loss during the first discharge cycle. For example, there has been observed a $\sim 700$ mAh/g irreversible capacity loss during the first discharge for SnO$_2$ electrode.\textsuperscript{35} This irreversibility is due to a sequential chemical reaction which will be discussed in Chapter 2.

1.4 Objective of This Study

As mentioned previously, metals in oxide forms have been shown to exhibit high capacity with good cyclability but have a major disadvantage of a large first cycle irreversibility loss. In an attempt to solve this problem, a new class of electrochemically active material, metal-metal oxide composite anodes produced by the partial reduction method, is explored in Chapter 2 of this thesis. Processing details, example systems and their electrochemical behavior with respect to microstructure are discussed. Better understanding of the micromechanical phenomena that lead to poor cyclability in Li-Me anodes is the primary objective of Chapter 3. The problem is investigated in the context of a fracture based failure criterion, and a comparison with direct SEM and TEM observations of cycled Li-Me anodes. Possible mechanisms leading to failure of Li-Me anodes along with experimental observations and analysis are presented. Selected
observations reported in this chapter, specifically the existence of an amorphous phase upon electrochemical cycling, are further investigated in Chapter 4. A new phenomenon that will be termed *electrochemically-induced solid-state amorphization* is proposed. Theoretical arguments and supporting experimental evidence for the phenomenon are included in this chapter. It is the aim of this thesis to deepen the understanding of the relationship between processing, microstructure, phase transformations, and subsequent electrochemical behavior in metal anodes.
1.5 References


1.6 Figures

Figure 1.1 Comparison of the energy storage capacity of various rechargeable battery systems.¹

Figure 1.2 Schematic of discharging and charging process for lithium-ion rechargeable batteries.³
Anode: carbon (graphite or amorphous)
Cathode: LiCoO$_2$, LiNiO$_2$, LiMn$_2$O$_4$
Binder: PVDF, Teflon™
Separator: PP, PE, PE sandwiched with PP
Electrolyte: LiPF$_6$, LiBF$_4$
Solvent: PC, EC, DEC, EMC, DMC
Conductive additives: carbon (acetylene black, graphite)
Can: Fe with Ni plated, Al, Stainless Steel

**Figure 1.3** A schematic diagram of a typical Li-ion battery along with the commonly used components.$^{3,5}$

**Figure 1.4** Ragone plot of specific energy versus specific power. It shows illustrated typical tradeoffs of batteries.$^4$
Chapter 2

Partially Reduced Metal-Metal Oxide Composites for Lithium-ion Battery

2.1 Introduction

As mentioned in Chapter 1, Li-Me anodes have poor cyclability due to disintegration upon cycling, which has been attributed to large volume changes during lithiation and delithiation (more on this on Chapter 3). Experiments on oxides containing metals that can alloy with lithium, such as Sn-B-P-O glass or SnO₂, have revealed much better cyclability over large numbers of cycles. This was thought to be in part due to the electrochemical reduction of the metal oxides by Li producing small finely dispersed metal particles embedded in a Li₂O matrix (see section 2.2.1).¹ ² The role of small isolated particles in reducing volumetric stresses upon lithiation and delithiation is discussed further in Chapter 3.

Despite the impressive improvements in cyclability of the oxide anodes, a major drawback is a large first cycle irreversible capacity loss attributed to the electrochemical reduction reaction of the metal oxide upon lithiation. In this chapter, metal-metal oxide composite anodes produced by a partial reduction method are explored as a possibility for maintenance of good cyclability and significant decrease in the first cycle irreversibility.
This approach allows tailored phase assemblages and microstructures to be prepared using simple, economical thermochemical processes and inexpensive starting materials. While partially reduced oxides have previously been investigated for a number of possible applications including selective absorption of solar energy, optical data storage and toughening of ceramics\(^3\text{-}^9\), it will be shown that this method can also be used to synthesize electrochemically active materials in several systems. Experiments are discussed for ternary oxides in the systems Sb-V-O, Sb-Mn-O, Ag-V-O and Sn-Ti-O.

2.2 Partial Reduction

2.2.1 Background on Partial Reduction

Partial reduction is a thermochemical process in which a ternary or higher order oxide (or nitride, sulfide, etc.) is subjected to conditions that reduce the most noble metal(s) but leaves the less noble metal(s) in an oxidized form:\(^9\)

\[
\begin{align*}
\text{Me}_3^I\text{Me}_5^{II}O_c & \xrightarrow{\text{partially}} a\text{Me}^I + \text{Me}_5^{II}O_y + (c-y)2\text{ O}_2 \\
\text{Reduced} &
\end{align*}
\]  

(2.1)

Here \(\text{Me}^I\) is more noble than \(\text{Me}^{II}\) (\(\text{Me}^I\) lies above \(\text{Me}^{II}\) on the Ellingham diagram (Fig. 2.1)\(^{10}\)). Depending on the starting composition, the relative diffusion rates of oxygen and the cations, and the phase makeup (single or multiphase) of the material, either internal reduction wherein the reduced specie precipitates inside an oxide matrix, or external reduction wherein the reduced metal forms at the outer surface, can occur.\(^9\) Quantitative analysis of internal vs. external partially reduction has been explored in detail for systems with slow oxygen diffusion by Schmalzried and Backhaus-Ricoult.\(^9\)
2.2.2 Partial Reduction Approach

Our objective was to produce fine particles of a lithium-active metal, Me\textsuperscript{1}, enclosed within or dispersed amongst particles of a metal-oxide matrix Me\textsuperscript{II}_bO\textsubscript{y}. The matrix itself may or may not be lithium active. Materials made by this process can have a number of advantages:

1) First-cycle irreversibility can be reduced since the electrochemically-driven displacement reactions that Li\textsubscript{2}O forms as a byproduct upon first lithium insertion\textsuperscript{6} can be avoided. It is believed that the insertion of lithium into metal oxides such as SnO\textsubscript{2} does not involve an intercalation process, but a process involving alloying of Li with the metal.\textsuperscript{2} The metal oxide has to be electrochemically reduced before alloying with Li. These displacement reactions are typically irreversible or poorly reversible.

\[
\begin{align*}
    \text{Me}_x\text{O} & \xrightarrow{2\text{Li}^+} \text{Li}_2\text{O} + x\text{Me} & \xrightarrow{2x\text{Li}} \text{Li}_{2x}\text{Me} + \text{Li}_2\text{O} \\
\end{align*}
\]

(2.2)

Li that was inserted initially reduces the metal oxide and forms Li\textsubscript{2}O. Li\textsubscript{2}O formed irreversibly at this step contributes to the loss of capacity after the first discharge. If the first step at which Li reduces the metal oxide is eliminated, Li can alloy with the metal directly,

\[
\begin{align*}
    (\text{Me}^1 - \text{Me}^{\text{II}})_b\text{O}_y & \xrightarrow{\text{partially reduced}} \text{Me}^1 + \text{Me}^{\text{II}}_x\text{O}_z & \xrightarrow{\text{Li}^{\text{insertion}}} \text{Li}_x\text{Me}^1 + \text{Me}^{\text{II}}_z\text{O}_z \\
\end{align*}
\]

(2.3)

and the irreversible capacity loss can be decreased.
2) Accommodation of Volume Changes

Ultrafine metal particles, which appear to better tolerate cyclic volume changes than coarser particles or bulk metal,\textsuperscript{1,11,12} can be produced. Partial reduction has been shown to produce metal particles as small in diameter as a few nanometers.\textsuperscript{7} Furthermore, volume shrinkage of the metal oxide upon reduction can provide room for the subsequent expansion of the metal upon lithiation (Fig. 2.2). It can be seen from Table 2.1 that the total volume change from starting oxide to lithiated compound can be almost zero for some systems.

3) Improvements in chemical compatibility between cell components

Passivating layers are known to exist between pure elemental negative electrodes and liquid electrolytes. The subsequent dendrite formation causes a non-uniform current density distribution at the electrode/electrolyte interface and increases interfacial impedance leading to electrical breakdown during cycling.\textsuperscript{13,14} For a partially reduced mixed oxide in those instances where internal reduction is achieved, the active metal particles are embedded within the oxide matrix and do not directly contact the electrolyte. Since the desired oxide will typically be a transition metal oxide (see below), most of which are more stable in contact with organic liquid electrolytes than the metals, interfacial reaction layer problems can be diminished. Moreover, as will be presented in Chapter 3, one of the causes of failure of metal anodes comes from chemical degradation due to metal and electrolyte compatibility. Where internal reduction of a partially reduced mixed oxide is achieved, the active metal particles can be isolated from the electrolyte by an oxide that is more chemically compatible.
4) High Electronic and Ionic Conductivity

Transition metal oxides are among the most attractive candidates for the host metal oxide $\text{Me}^{\text{II}}_x\text{O}_2$, since many can be tailored to have high electronic and lithium ionic conductivity, especially when heat treated under reducing conditions. Most lithium intercalation cathodes are based on chemically-similar transition metal oxides. Having an electronically conductive host can reduce or eliminate the conductive additive used in electrode formulations.

2.2.3 Selection Criteria for Partially Reduced Anodes

Because most metals studied to date alloy at voltages $<1$ V relative to lithium metal, they are primarily suitable for the anode in rechargeable lithium batteries. Criteria for choosing a starting mixed oxide ($\text{Me}^{\text{I}}\text{-Me}^{\text{II}})_x\text{O}_2$ include the following:

- For high energy density, $\text{Me}^{\text{I}}$ should alloy with Li at a low voltage with respect to lithium metal and high Li/$\text{Me}^{\text{I}}$ ratio. Low atomic mass and high density for both $\text{Me}^{\text{I}}$ and $\text{Me}^{\text{II}}_x\text{O}_2$ are preferred to obtain high gravimetric and volumetric capacity.

- The oxides of $\text{Me}^{\text{I}}$ and $\text{Me}^{\text{II}}$ should form an intermediate compound or solid solution. Immiscibility can be useful if fine-scale phase separation can be obtained.$^{10}$

- The Gibbs free energy of oxidation for $\text{Me}^{\text{I}}$ must be reasonably less negative than that of $\text{Me}^{\text{II}}$ so as to allow latitude in processing temperature and atmosphere. That is, $\text{Me}^{\text{I}}$ should lie significantly above $\text{Me}^{\text{II}}$ on the Ellingham diagram.

- The net molar volume change from reduction of the starting oxide $\text{Me}^{\text{I}}_x\text{O}_b$ through lithiation to the compound $\text{Li}_x\text{Me}^{\text{I}}$ should be as low as possible (Fig. 2.2).

- $\text{Me}^{\text{II}}_x\text{O}_2$ is preferably a good electronic and lithium ion conductor.
• Low-cost and non-toxic metals and metal oxides are preferred.

The generality of our approach is indicated by the fact that upon searching the JCPDS data base\textsuperscript{15}, over 100 compounds have been found that meet most or all of the above criteria (Appendix A). However, as we show, the electrochemical performance especially upon extended cycling depends also on the microstructure that is obtained. Within the general approach of partial reduction, we have identified three specific strategies for obtaining fine dispersions of the metal within an oxide matrix:

1) The concentration and relative diffusivity of the lithium-active metal can be selected to obtain internal vs. external reduction, in oxides with low oxygen diffusivity\textsuperscript{9}

2) Systems of high oxygen diffusivity for which internal reduction is always expected can be selected.

3) Phase-separation can be conducted prior to reduction in order to confine the reduced metal phase.

In this chapter we illustrate these approaches using several examples.

2.3 Selected Systems

Table 2.2 lists the five example systems that were investigated. Each has different structural, composition and transport characteristics which result in different microstructures and electrochemical characteristics. In the course of this thesis, approximately 300 individual samples were prepared from these starting compounds to study the partial reduction process and resulting electrochemical behavior.
2.3.1 SbVO₄ and Sb₂Mn₂O₇

Sb is of interest for lithium storage since it can alloy up to 3 Li per Sb atom, giving a theoretical charge capacity of 661 Ah/kg (4415 mAh/cm³) at a voltage plateau of 0.94-0.96 V¹⁶ relative to Li metal. The volumetric expansion upon lithiating Sb is large, being a factor of 1.97 for forming Li₂Sb and 2.35 for forming Li₃Sb. However, interestingly, the molar volumes of Sb₂O₅ and Li₃Sb are almost equal, resulting in nearly zero volume change upon reducing the oxide to Sb metal followed by lithiation to Li₃Sb (Table 2.1). We compare the starting oxides SbVO₄ and Sb₂Mn₂O₇ because of their different crystal structures and transport characteristics. SbVO₄ has the rutile structure in which cation diffusion is expected to be more rapid than oxygen diffusion; hence the kinetics of partial reduction analyzed by Schmalzried et. al⁹ should apply. Due to the high Sb fraction, external reduction may occur. This compound has been widely used in catalytic applications.¹⁷ Sb₂Mn₂O₇, in contrast, has the distorted fluorite structure¹⁸ in which oxygen diffusion should be much more rapid than cation diffusion once some reduction occurs, resulting in formation of oxygen vacancies. In this case, internal reduction is expected as long as the matrix remains intact. Here we will present additional results showing how control of the starting oxide particle size can be used to increase the fraction of internal metal. Analyses of the composite morphology before and after cycling have also been conducted.

2.3.2 AgVO₃ and Ag₂V₄O₁₁

Lithium is reported to alloy with Ag to form compounds LiAg, Li₁₀Ag₃, and Li₁₂Ag,¹⁹ thereby yielding potentially high storage capacities. In electrochemical tests,
Ag is found to alloy with Li at a low voltage of ~0.02-0.1 V for low concentrations;\textsuperscript{20} more highly lithiated alloys have not been obtained. Both AgVO\textsubscript{3} and Ag\textsubscript{2}V\textsubscript{4}O\textsubscript{11} are compounds in which oxygen diffusion is expected to be slow relative to cation diffusion, but the lower Ag concentration in the latter should promote internal reduction.\textsuperscript{9} AgVO\textsubscript{3} is available commercially and Ag\textsubscript{2}V\textsubscript{4}O\textsubscript{11} is a well-known cathode material for primary lithium cells used in medical implant applications. After partial reduction, the vanadium oxide matrix is attractive due to its high lithium ion and electronic conductivity.

2.3.3 Sn\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{2}

(Sn,Ti)O\textsubscript{2} was studied as an example of metal confinement due to phase separation. SnO\textsubscript{2} lies well above TiO\textsubscript{2} on the Ellingham diagram and can be preferentially reduced. Sn is a well-studied metal anode which can alloy up to 4.4 Li per Sn, while TiO\textsubscript{2} is known to have good ionic and electronic conductivity.\textsuperscript{21} While a complete rutile solid solution of TiO\textsubscript{2} and SnO\textsubscript{2} can be achieved at high temperatures (T>1430° C for the equimolar composition),\textsuperscript{22} at lower temperature there is a miscibility gap that is nearly symmetrical in composition (Fig 2.3)\textsuperscript{22}. Within the spinodal regime, finely-divided lamellar microstructures with layers as fine as 20 nm thickness, alternatively rich in SnO\textsubscript{2} and TiO\textsubscript{2}, can be obtained.\textsuperscript{22,23} Two-phase microstructures of varying length scales can be created, within which the SnO\textsubscript{2}-rich phase can be preferentially reduced to Sn metal. Doping influences both decomposition kinetics\textsuperscript{22,23} and electrical properties; it is known that most subvalent cations in TiO\textsubscript{2} form deep acceptor levels resulting in electronically insulating oxides at room temperature, while supervalent cations tend to form shallow donor levels yielding good electronic
Both microstructure and electronic conductivity can therefore be widely manipulated in this system through control of composition and processing conditions.

2.4 Experimental Procedure

2.4.1 Preparation of Starting Compounds

SbVO₄, Sb₂Mn₂O₇, and Ag₂V₄O₁₁ were prepared using solid state reaction processes beginning with reagent grade oxides or carbonates. SbVO₄ was prepared by ball milling a 1:1 molar ratio of Sb₂O₃ (99.3% Alfa Aesar, Ward Hill, MA, USA) with V₂O₅ (99.6% Aldrich, Allentown, PA, USA) in a polypropylene bottle using Teflon® balls for 24 hours. The mixture was then fired in air at 700°C for 24 hours resulting in a single phase of SbVO₄. Sb₂Mn₂O₇ was prepared by ball milling a 1:2 molar ratio mixture of Sb₂O₃ (99.3% Alfa Aesar) and MnCO₃ (99.9% Alfa Aesar), then calcining and reacting in air at 600°C for 7 hours, 650°C for 4 hours, 750°C for 5.5 hours, 1100°C for 21 hours.

Ag₂V₄O₁₁ powder was prepared by ball milling a 1:2 molar mixture of Ag₂O (99% Alfa Aesar) and V₂O₅ (99.6% Aldrich). Single phase Ag₂V₄O₁₁ was found after reacting the mixture in O₂ atmosphere at 500°C for 10 hours. The AgVO₃ starting powder was purchased from Aldrich.

Phase-separated SnO₂ – TiO₂ composites were obtained by first synthesizing a (Sn,Ti)O₂ solid-solution powder and then carrying out thermal decomposition. The compositions studied had a 1:1 molar ratio of Sn:Ti, to which Al³⁺ (0.8 mole%) and Ta⁵⁺ (0.6-1.0 mole%) were added as the acceptor and donor dopants respectively to influence
decomposition and electrical properties. The starting powder was prepared via either a co-precipitation or a solid state reaction method. For the powder made by co-precipitation method, (Sn,Ti)O₂ doped with 0.8 mole% Al³⁺ or 0.6-1 mole% Ta⁵⁺ was prepared from the metal chlorides using a process described by Maruyama et al.²². Stoichiometric amounts of high purity TiCl₄ (99.999% Alfa Aesar) and SnCl₄ (99.95% Alfa Aesar) solution were poured over ice, forming an aqueous solution while preventing a highly exothermic reaction. While stirring, the solution was doped with the desired amount of AlCl₃.6H₂O (99.995% Puratonic Grade, Alfa Aesar) or TaCl₅ (99.99% Alfa Aesar). An addition of 50% NH₄OH (Alfa Aesar) in water initiated the precipitation of a white viscous gel. The precipitate was washed with distilled water and the supernatant decanted several times, then freeze-dried. The resulting powder was calcined at 600°C for 1.5 hours to obtain the solid solution powder. In the solid state reaction method, stoichiometric amounts of SnO₂ (99.9% Alfa Aesar) and TiO₂ (99.9% Alfa Aesar) doped with Al(OH)₃ (Alfa Aesar) or Ta₂O₅ (99.993% Puratonic Grade, Alfa Aesar) were ball-milled as described above, then heated in air to 1475°C, a temperature above the miscibility gap maximum (1430°C), for 12 hours to obtain a solid solution oxide. For starting powder prepared by either method, decomposition heat treatments were subsequently carried out at temperature between 900°C-1000°C, for 12-880 hours to allow phase separation. The rate of phase separation is highly sensitive to composition and temperature in this system. XRD was used to confirm that phase separation had occurred prior to partial reduction in each instance.
2.4.2 Partial Reduction Heat Treatments

For partial reduction, a small amount of each ternary oxide powder (~0.4-2g) was heated in an alumina boat (with powder depth ~2mm) in a tube lined furnace under temperature and atmospheric conditions given later in the Results section for each material. Both buffered CO/CO₂ gas mixtures and unbuffered pure H₂ gas (BOC Gas, Murray Hill, NJ, USA) at 1 atm total pressure were used. In the case of CO/CO₂ gas mixture, temperature and oxygen activity can be selected to reduce only the more noble metal. In the case of hydrogen gas, although the specific oxygen partial pressure could not be determined, it allowed us to carry out the reduction process at low temperature (<500°C) without the deposition of carbon observed in the case of CO/CO₂.

2.4.3 Microstructural Characterization

X-ray diffraction (Rigaku RU300, Cu-Kα radiation, Rigaku/MSC, The Woodlands, TX, USA) and weight loss were conducted of each of the samples before and after partial reduction heat treatments to determine the phases present, and the extent of reduction. JEOL 2000FX and 2010FX (JEOL, Ltd., Tokyo, Japan) transmission electron microscopes (TEM), a Fisons HB603 (Fiscon Instruments, VG Microscopes, East Grinstead, UK) scanning transmission electron microscope (STEM), a Philips XL30 (FEI/Philips, Hillsboro, OR, USA) environmental scanning electron microscope (ESEM) and a JEOL JSM-6320FV (JEOL, Ltd., Tokyo, Japan) field emission gun scanning electron microscope were used to characterize the sample microstructures and identify phases.
2.4.4 Electrochemical Characterization

Electrodes consisting of 70-88 wt% of the sample, 5-10 wt% carbon additive (Super P, Chemetals Inc, Easthampton, MA USA.; acetylene black, 99.9%, Alfa Aesar, or graphite, 1-2 μm, Aldrich), and 10-20 wt% of polyvinylidene fluoride binder (Aldrich) were prepared. These were mixed with γ-butyrolactone solvent (98%, Alfa Aesar) and either cast onto a sheet of Cu foil, or dried and then pressed at 4000 kg/cm³ into ¼” diameter pellets. All electrodes were assembled in stainless steel cells using Li foil (0.75 mm, Alfa Aesar) as the counter electrode, EC:DMC (1:1 by weight) with 1 M LiPF₆ (EM Science, Norwood, OH, USA) as the electrolyte, and Celgard™ 2400 (Celgard, Inc. Charlotte, NC, USA) as the separator. All cell assembling was done in an Ar-filled glovebox with < 3 ppm O₂ and H₂O. Li foil was punched out into a 3/8” disk and placed onto the bottom of the cell. A piece of ½” diameter Celgard™ separator was placed on top of the Li foil. 3-4 drops of the electrolyte were then added before the tested pellet was placed onto of the separator. Additional 6-7 drops of the electrolyte were added to ensure that the entire pellet was wet with electrolyte. A metal contact was placed onto the tested pellet, and the cell was finger-tightly closed. Each end of the cell was connected to an electrical lead, and was placed in a sealed jelly jar before removing from the glovebox for testing. Cycling was conducted at room temperature. The Super P carbon additive made a significant contribution to the first-cycle irreversible capacity loss and reversible capacity of the electrodes. When formulated into electrodes and tested separately, up to 550 mAh/g of carbon and up to 80 mAh/g irreversible capacity was seen on the 1st discharge at 0.7-1.3 V range. The capacity data was corrected by subtracting the capacity contribution of the added carbon from the total electrode capacity.
2.5 Results and Discussion

2.5.1 SbVO₄ and Sb₂Mn₂O₇

Partial reduction was successfully carried out at very low temperatures; complete reduction of the antimony oxide fraction to Sb metal could be accomplished at temperatures as low as 400°C (4h, H₂) for SbVO₄, and 360°C (18h, H₂) for Sb₂Mn₂O₇. Figures 2.4 and 2.5 show XRD patterns of the unreduced and partially reduced SbVO₄ and Sb₂Mn₂O₇ respectively. SEM and TEM analyses showed a dramatic difference in Sb precipitate size between the two composites. Reduced SbVO₄ showed external Sb metal precipitates of octahedral morphology as large as 20 μm mixed with vanadium oxide phase, while the reduced Sb₂Mn₂O₇ exhibited much finer Sb particles, ranging from ~2 μm to ~20 nm as observed by TEM, mixed with MnO phase (Figs. 2.6a, b). The finer precipitate size occurred despite a longer reduction time for Sb₂Mn₂O₇. We believe that Sb metal precipitation occurred internally in the distorted fluorite due to its high oxygen diffusivity, causing Sb coarsening to be inhibited. In contrast, external reduction appears to occur throughout for the slow oxygen diffusion system SbVO₄, leading to coarse metal particles. In the case of Sb₂Mn₂O₇, even though the precipitated metal is primarily internal, a certain amount of Sb lying within a characteristic diffusion length of the surface can diffuse to the surface and form external precipitates of Sb metal.

In order to obtain samples with higher fraction of Sb internal precipitates and finer Sb particle size, the Sb₂Mn₂O₇ particle size prior to partial reduction was increased through thermal coarsening. This lowers the specific surface area and is expected to decrease the fraction of external precipitates. The as-synthesized Sb₂Mn₂O₇ was further heat-treated for various times and at various temperatures, after which the particle size
was examined using SEM. Results presented here are for heat treatment in air at 1300°C for 8 hours. A significant increase in the average particle size from less than 1 μm in the starting material to 6.5 μm after coarsening was observed. The coarsened Sb$_2$Mn$_2$O$_7$ was then subjected to partial reduction at 420°C for 24 h in H$_2$. SEM images of the coarsened oxide and partially reduced Sb-MnO composite (Fig. 2.7) show that a high fraction of Sb internal precipitates is obtained.

Figures 2.8a and 2.8b show typical voltage profiles for the Sb-V$_2$O$_3$ and Sb-MnO composites, respectively. The average voltage between charge and discharge plateaus was found to be ~0.97 V, and closer examination revealed two closely-spaced plateaus upon discharge, corresponding to the formation of Li$_2$Sb and Li$_3$Sb respectively.\textsuperscript{16} Upon cycling, the coarse-grained Sb-V$_2$O$_3$ composite behaves like a mixture of the two phases without a tailored microstructure. The composite has an initial capacity of 415 mAh/g that is close to the theoretical value of a 1:1 molar ratio of Sb:V$_2$O$_3$ (409 mAh/g), assuming V$_2$O$_3$ to be inactive in this voltage range. However, rapid capacity fade in the first several cycles was observed for the coarse Sb metal in this sample (Fig. 2.9a). The Sb$_2$Mn$_2$O$_7$-derived material with its finer metal dispersion exhibits much better cyclability (Fig. 2.9b). The sample with a still higher fraction of fine internal Sb precipitates, shown in Fig. 2.7, exhibited even better capacity retention (Fig. 2.9c). These cells did show lower coulombic efficiency, and a surprising feature of sudden fade after about 20 cycles (Fig. 2.9b, 2.9c). Further investigation indicated that the sudden capacity fade was a cell failure and not an intrinsic property of the tested material. After the sudden capacity fade of cell Sb-MnO #1 at the 20th to 25th cycle and Sb-MnO #2 at the 20th to 22nd cycle, the cells were disassembled and reassembled using a new lithium
electrode and electrolyte. We then found that the charge (lithium extraction) capacities were mostly restored. Furthermore, the cumulative inefficiencies found in these samples are much larger than the irreversible storage capacities possible from the materials in the electrode. It is also seen that the inefficiency increases again after the rebuilding of the cells (Fig. 2.9b and 2.9c). This indicates that the coulombic inefficiency cannot be attributed to the tested material alone but some other side reaction due to the Li metal electrode or the electrolyte, such as SEI formation or electrolyte decomposition.

SEM examination of the microstructure of the internally reduced Sb-MnO composite after electrochemical cycling reveals that the initial morphology of Sb metal embedded in the MnO matrix was retained (Fig. 2.10), although some fracturing of the matrix does occur. The improved capacity retention upon cycling of this material is attributed to the preservation of the internal reduction morphology, which helps to maintain connectivity between the active metal and the oxide matrix through cyclic volumetric expansion and contraction of the metal. In Chapter 3, it has been shown that Sb metal powder cycled in the same electrolyte system undergoes systematic disintegration into nanocrystalline metal particles. This is clearly avoided when the Sb metal is contained within an oxide matrix, as in the internally-reduced Sb-MnO composites.

The theoretical charge capacity for Sb-MnO obtained by reducing Sb$_2$Mn$_2$O$_7$ is 417 mAh/g (2570 mAh/cm$^3$, assuming the theoretical density of 6.16 g/cm$^3$). The two Sb$_2$Mn$_2$O$_7$-derived samples in Fig. 2.9b and 2.9c show reversible capacities of ~300 mAh/g (1850 mAh/cm$^3$) and ~225 mAh/g (1385 mAh/cm$^3$) respectively. In the latter case, the reduced capacity is attributed to incomplete reduction of the Sb oxide in the
starting material. This was clearly evident in the amount of weight loss and the presence of retained fluorite phase in the reduced sample observed by XRD (From the measured weight loss before and after reduction, it was calculated that 76% of the starting Sb-O was reduced to Sb metal, assuming that each mole of the partially reduced Sb$_2$Mn$_2$O$_7$ gives 2 moles of Sb metal and 2 moles of MnO upon reduction.). With further development, a reversible gravimetric capacity of $\sim$350 mAh/g corresponding to volumetric capacity of $\sim$2150 mAh/cm$^3$ should be possible for this system. The comparison between SbVO$_4$ and Sb$_2$Mn$_2$O$_7$ clearly demonstrates the influence of the structure and transport properties of the starting compound on the microstructure obtainable through partial reduction, and subsequently on the electrochemical properties.

2.5.2 AgVO$_3$ and Ag$_2$V$_4$O$_{11}$

XRD patterns showing AgVO$_3$ partially reduced at 360°C for 6 hours in H$_2$, Ag$_2$V$_4$O$_{11}$ reduced at 500°C for 4 hours in H$_2$ are presented in Fig 2.11a and 2.11b, respectively. Only peaks for Ag metal are seen; the vanadium oxide is present as an amorphous phase. Externally precipitated Ag particles were observed using TEM and STEM for the partially reduced AgVO$_3$, whereas the partially reduced Ag$_2$V$_4$O$_{11}$ exhibited fine internal Ag precipitates of < 20nm thickness within the vanadium oxide (Fig. 2.12a). The occurrence of internal reduction in the latter case may be due to the lower Ag concentration, as expected from Schmalzried’s model. Cycling data for Ag$_2$V$_4$O$_{11}$ reduced at 500°C for 4 hours in H$_2$ are shown in Fig 2.12b. The reversible capacity of $\sim$50 mAh/g is close to the theoretical capacity of the composite if it is assumed that only the Ag alloys with Li, and that alloying up to 1 Li per Ag atom occurs.
This indicates that the higher lithium alloys (Li$_{10}$Ag$_3$, Li$_{12}$Ag) are not formed within the voltage range 0.005-2V (to our knowledge this is the first time this has been demonstrated). A large first-discharge capacity is also observed in this instance, which is probably due to electrochemical activity of the highly disordered vanadium oxide phase between 1.75-3 V. Ag$_2$V$_4$O$_{11}$ is thus another example of a system with good cyclability achieved due to internal reduction of the metal. However, due to the low overall charge capacity of this composite system, it was not pursued further.

2.5.3 (Sn$_{0.5}$Ti$_{0.5}$)O$_2$

Figures 2.13a and 2.13b shows TEM images of phase-separated microstructures in the Sn$_{0.5}$Ti$_{0.5}$O$_2$ system, showing the SnO$_2$-rich (dark) and TiO$_2$-rich (light) lamellae. The Al$^{3+}$ doped sample has lamellar spacing of 10-20 nm after being decomposed at 900°C for 12h in air, while the Ta$^{5+}$ doped sample has a finer spacing of <10 nm despite being decomposed at a higher temperature and longer time of 1000°C for 325h in air. This is consistent with doping effects seen in previous studies of this material.$^{22,23,25}$ Figures 2.13c and 2.13d shows corresponding images of the samples after partial reduction (at 360°C for 15h in H$_2$ for Al-doped, and 450°C for 4h in H$_2$ for Ta-doped). A large fraction of the reduced Sn metal is captured between TiO$_2$-rich platelets, at a particle size of ~10 nm. However, a significant fraction of the reduced Sn also formed external spherical particles with a distribution of sizes up to 0.5 μm diameter. Unlike the cases of Sb and Ag, partial reduction was carried out above the melting point of Sn metal (232°C). The coarser Sn particles may have coalesced from smaller droplets or coarsened through vapor phase transport. Thus these composites contain a distribution of Sn
particle sizes ranging from ~10 nm to ~0.5 μm, with a larger average size occurring in the Al-doped samples. Based on the weight loss during partial-reduction, it was determined that only 33% of the total SnO₂ had been reduced to Sn metal for the Al doped sample (partially reduced at 360°C for 15h in H₂), and 56% for the Ta doped sample (partially reduced at 450°C for 4h in H₂). This may be due to slow reduction kinetics at the temperatures used, as well as retention of ~10% SnO₂ in solid solution in the TiO₂, as indicated by the equilibrium phase diagram.²³

Figure 2.14 compares the electrochemical behavior of the un-reduced Al-doped sample, its partially reduced Sn-TiO₂ counterpart, and the partially reduced Ta-doped Sn-TiO₂ composite. The un-reduced (Sn,Ti)O₂ exhibits the largest first-cycle irreversibility (78%). Improvement in the first-cycle irreversibility was observed for both of the partially reduced samples (64% for Al-doped and 55% for Ta-doped). A large fraction of the irreversibility is interpreted as being due to the electrochemical reduction of the residual SnO₂ to Sn. Solid electrolyte interface (SEI) formation probably also contributes to the irreversible capacities observed during the 1st cycle because the capacity loss is much larger than the un-reduced SnO₂ alone can produce. The larger plateau at ~1 V in the un-reduced sample (Fig. 2.15a) is consistent with the reduction of SnO₂ by Li,²⁶ and the charge capacities were below the theoretical value of 594 mAh/g (3360 mAh/cm³) expected for Sn₀.₅Ti₀.₅O₂ which has been fully reduced to a 1:1 molar ratio of Sn:TiO₂.

For the Al-doped composition, both the starting oxide and the partially-reduced composite exhibit poor cyclability as seen in Figs. 2.14a and 2.14b. The rapid capacity fade is attributed to a majority of the reduced Sn being in the form of coarse particles. Note also that a large polarization develops during the first few cycles. In comparison,
the Ta-doped sample exhibits lower first-cycle irreversibility, better capacity retention, and lower polarization (Fig. 2.14c). The lower polarization compared to Fig. 2.14b is attributed to the higher electronic conductivity of donor-doped TiO$_2$\textsuperscript{21,24}. Upon narrowing the voltage range of the Ta-doped sample to 0.3-1.2V, a decrease in capacity from 300 to 200 mAh/g (1000 mAh/cm$^3$) was seen but the cyclability further improved (Fig. 2.15). After about 50 cycles, the capacity stabilized at $\sim$100 mA/g (Fig. 2.16). It appears that the earlier cycles cause the systematic loss of capacity from larger Sn particulates, while the finer particles in the particle size distribution continue to cycle reversibly.

This example demonstrates the concept of partial reduction of a micro phase-separated mixture of oxides to produce an electrochemically active composite. While the storage properties for the Sn-Ti-O system are not yet sufficient for practical use, we believe that further development of this concept in related systems can narrow the size distribution of active metal particles and result in improved properties.

2.6 Conclusions

The partial reduction of mixed oxides has been studied in several systems as a new approach to synthesizing electrochemically-active metal-ceramic composites. By choosing oxide compounds with suitable crystal structures and active cation concentrations, fine internal dispersions of lithium-active metals can be obtained which show markedly improved resistance to cycling fade compared to coarser, externally precipitated metal. In these materials, improved cycling is attributed to both a reduction in metal particle size and the passivation of the metal particles by the surrounding oxide
matrix. While first-cycle irreversibility due to presence of residual lithium-active oxide phases needs to be further improved, reversible gravimetric capacities up to 350 mAh/g and volumetric capacities up to 2000 mAh/cm³ have been demonstrated in the systems studied to date. From the processing viewpoint, this approach is attractive since inexpensive starting materials and relatively simple, scalable, thermochemical processes can be used.
2.7 References


15. JCPDS-International Centre for Diffraction Data.


2.8 Tables

Table 2.1 Percentage of molar volume change of various metal oxides to their metal followed by lithiating to Li-Me alloys.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Metal</th>
<th>Lithiated Compound</th>
<th>%Molar vol. increase from metal oxide to lithiated compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Al</td>
<td>LiAl</td>
<td>51.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li₂₂₅Al</td>
<td>161.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li₃Al</td>
<td>291.9</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>B</td>
<td>Li₁₂₅B</td>
<td>-5.6</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>Bi</td>
<td>Li₃Bi</td>
<td>74.7</td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>Sb</td>
<td>LiBi</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li₂Sb</td>
<td>27.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li₃Sb</td>
<td>52.5</td>
</tr>
<tr>
<td>Sb₂O₅</td>
<td>Sb</td>
<td>Li₂Sb</td>
<td>-15.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li₃Sb</td>
<td>0.4</td>
</tr>
<tr>
<td>SnO₂</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Li₂₆Sn</td>
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<tr>
<td></td>
<td></td>
<td>Li₃₄Sn</td>
<td>123.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li₄₄Sn</td>
<td>168.7</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn</td>
<td>LiZn</td>
<td>25.7</td>
</tr>
</tbody>
</table>
Table 2.2  Examples of mixed metal oxides which have been partially reduced to form metal-ceramic composite anodes. Their structure, composition and transport characteristics are relevant to the microstructures obtainable through thermochemical reduction.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Diffusivity</th>
<th>Observed Characteristic and Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbVO₄</td>
<td>Rutile</td>
<td>( D_{\text{cations}} &gt; D_{\text{oxy}} ) ( D_{\gamma3+} &gt; D_{\text{Sb}5+} )</td>
<td>External reduction as expected</td>
</tr>
<tr>
<td>Sb₂Mn₂O₇</td>
<td>Distorted Fluorite</td>
<td>( D_{\text{oxy}} &gt; D_{\text{cations}} )</td>
<td>Internal reduction</td>
</tr>
<tr>
<td>AgVO₃</td>
<td>Perovskite</td>
<td>( D_{\text{cations}} &gt; D_{\text{oxy}} ) ( D_{\text{Ag}1+} &gt; D_{\gamma5+} )</td>
<td>External reduction due to high Ag/V ratio</td>
</tr>
<tr>
<td>Ag₂V₄O₁₁</td>
<td>Bronze (corner-shared octahedra)</td>
<td>( D_{\text{cations}} &gt; D_{\text{oxy}} ) ( D_{\text{Ag}1+} &gt; D_{\gamma5+} )</td>
<td>Internal reduction</td>
</tr>
<tr>
<td>(Sn,Ti)O₂</td>
<td>Rutile</td>
<td>( D_{\text{cations}} &gt; D_{\text{oxy}} )</td>
<td>Internal reduction due to phase confinement</td>
</tr>
</tbody>
</table>
2.9 Figures

Figure 2.1. Ellingham diagram of various of oxides.\textsuperscript{10}
Figure 2.2  Schematic illustrating partial reduction of a mixed oxide producing an internal metal precipitate $\text{Me}^1$ of reduced volume in an oxide $\text{Me}^{\text{II}}_x\text{O}$, followed by lithiation of the metal to an alloy $\text{Li}_x\text{Me}^1$ with accompanying volume expansion.

Figure 2.3  $\text{SnO}_2$-$\text{TiO}_2$ phase diagram showing a miscibility gap below $1430^\circ\text{C}$ at the equimolar composition.\textsuperscript{22}
Figure 2.4 X-ray diffraction patterns of the starting oxides $\text{SbVO}_4$ and $\text{SbVO}_4$, partially reduced at $400^\circ\text{C}$ for 4 h in $\text{H}_2$. 
Figure 2.5  X-ray diffraction patterns of the starting oxides $\text{Sb}_2\text{Mn}_2\text{O}_7$, and $\text{Sb}_2\text{Mn}_2\text{O}_7$ partially reduced at 360°C for 18 h in $\text{H}_2$. 
Figure 2.6  SEM images of a) partially reduced SbVO$_4$ (400°C for 4 h in H$_2$) and b) partially reduced Sb$_2$Mn$_2$O$_7$ (360°C for 18 h in H$_2$). Coarse externally precipitated Sb is seen for the SbVO$_4$ derived sample, while much finer internal precipitates of Sb are found for Sb$_2$Mn$_2$O$_7$, in which oxygen diffusion is much faster than cation diffusion.
Figure 2.7  SEM image of a partially reduced $\text{Sb}_2\text{Mn}_2\text{O}_7$ (420°C for 24 h in $\text{H}_2$) with initially large starting $\text{Sb}_2\text{Mn}_2\text{O}_7$ particle size and its cross-sectional backscattering SEM image, showing internally precipitated Sb metal.
Figure 2.8 Voltage vs. capacity curve of a) Sb-V\textsubscript{2}O\textsubscript{3} produced by partial reduction of SbVO\textsubscript{4} (400\textdegree C for 4 h in H\textsubscript{2}), tested at 10 mA/g, and b) Sb-MnO\textsubscript{2} produced by partial reduction of Sb\textsubscript{2}Mn\textsubscript{2}O\textsubscript{7} (360\textdegree C for 18 h in H\textsubscript{2}), tested at 14 mA/g.
Figure 2.9 Capacity vs. cycle number of a) Sb-V$_2$O$_3$ sample with large external Sb precipitates (0.5-1.5V, 10 mA/g). Note the rapid fade in the first few cycles. b) Sb-MnO (sample from Fig. 2.6b) with finer external precipitates as well as internally reduced Sb (0.7-1.3V, 14 mA/g), and c) Sb-MnO (sample from Fig. 2.7) with predominantly internal Sb particles (0.7-1.3V, 6 mA/g).
Figure 2.10 Cross-sectional backscattering SEM image of the Sb-MnO composite after electrochemical cycling (50 cycles between 0.7-1.3V). The microstructure of Sb embedded in MnO is retained.
Figure 2.11 XRD patterns of a) AgVO$_3$, partially reduced at 360°C for 6 hours in H$_2$, and b) Ag$_2$V$_4$O$_{11}$, partially reduced at 500°C for 4 hours in H$_2$. 
Figure 2.12 a) STEM image of internally precipitated Ag for Ag$_2$V$_4$O$_{11}$ partially reduced at 500°C for 4h in H$_2$. b) Cycling data for the partially reduced Ag$_2$V$_4$O$_{11}$ (20 mA/g).
Figure 2.13 Bright-field TEM images of doped Sn$_{0.5}$Ti$_{0.5}$O$_2$: a) 0.8 mole% Al-doped phase separated at 900°C, 12h, and b) partially reduced at 360°C, 15h in H$_2$. c) 1 mole% Ta-doped composition phase separated at 1000°C, 325h, and d) partially reduced at 450°C, 24h in H$_2$. 
Figure 2.14 Comparison of the cycling behavior of a) phase-separated unreduced; b) Al$^{3+}$ doped partially reduced and; c) Ta$^{5+}$ doped partially reduced (Sn$_{0.5}$Ti$_{0.5}$)O$_2$. Rapid capacity fade was found in the unreduced and reduced Al$^{3+}$ doped with coarse Sn precipitates while the reduced Ta$^{5+}$ doped partially reduced sample exhibits better cyclability due to finer Sn microstructure and lower polarization due to better conductivity.
Figure 2.15 Cycle vs. capacity of phase-separated unreduced, Al$^{3+}$ doped partially reduced, and Ta$^{5+}$ doped partially reduced ($Sn_{0.5}Ti_{0.5}$)$_2O_2$ with the best cyclability found in the Ta$^{5+}$ doped sample with fine Sn particles.
Figure 2.16  Extended cycling of Ta doped Sn-TiO₂. Capacity drops is from 200 mAh/g to 100 mAh/g at approximately 12^{th} cycle due to coarse Sn particles with fine Sn particles continue to cycle reversibly.
Chapter 3

Failure Mechanisms in Lithiated-Metal Anodes

3.1. Introduction

As mentioned in Chapters 1 and 2, a major disadvantage of metal anodes is poor cyclablity, manifested in nearly complete capacity fade after a small number of charge-discharge cycles.\textsuperscript{1,2} This drawback has been attributed to mechanical fracture of the electrodes due to the large volume changes (Table 3.1) during lithiation and delithiation. Yang, \textit{et al.}\textsuperscript{3} reported improved cyclability in Li-Me anodes with small (< 1 \textmu m) initial particle size. In addition, as mentioned in Chapter 2, research on metal oxide anodes has revealed better cyclability for those systems, also attributed largely to small active metal particle size formed by internal electrochemical reduction. This finding has led to the exploration of nano-particle production methods for anode materials.\textsuperscript{4-11} The relative success of anodes containing smaller particles has been attributed to a reduction in overall stress.

In order to provide a criterion for particle size selection, Huggins and Nix\textsuperscript{12} have proposed a mechanistic model investigating the quantitative effect of particle size on resistance to mechanical failure during lithiation. Using an argument that the electrochemical lithiation must involve a heterogeneous distortion to generate internal stresses, they used a linear-elastic fracture mechanics model, based on a bilayer
geometry, to predict a critical particle size below which such failure would not occur. By assuming failure occurs during lithiation and using fracture of the substrate as the failure criterion, the critical particle size, \( h_c \), was predicted to follow the following relationship:

\[
h_c = \frac{23}{\pi} \left( \frac{K_{IC}}{Be_o} \right)^2 = \frac{23}{\pi} \left( \frac{3K_{IC}}{Be_T} \right)^2
\]  

(eq. 3.1)

When \( K_{IC} \) = fracture toughness (MPa m\(^{1/2}\))

\( B \) = bulk modulus of metal assuming the same value before and after lithiation

\( e_T \) = dilation = \( \Delta V/V \)

\( e_o \) = in plane strain = \( e_T/3 \)

In this study we tested the Huggins-Nix model, in which it is presumed that failure occurs during first insertion due to fracture of the underlying substrate under tension. If this were the case, vastly different behavior would be expected for metals with different mechanical properties (i.e. \( K_{IC} \)). We examined a range of lithiating metals with a variety of \( K_{IC} \) values (Table 3.1). Powder samples of each metal were studied, with a particle size distribution ranging from 45 \( \mu m \) down to 0.1 \( \mu m \), allowing examination of behavior as a function of particle size. Direct observations of the structure of the cycled metals were subsequently performed in order to understand the mechanisms of fracture.

### 3.2. Experimental Procedure

Powders of Ag (0.5-1 \( \mu m \), 99.9% Alfa Aesar, Ward Hill, MA, USA), Al (-325 mesh, 99.5% Alfa Aesar), Sn (-325 mesh, 99.8% Alfa Aesar), Sb (-325 mesh, 99.5% Alfa...
Aesar) and Si (-325 mesh, 99.95% Alfa Aesar) were used. The tested electrodes were prepared by mixing 80-90 wt% of the metal powder, 0-15 wt% Super P (Chemetal, Inc., Easthampton, MA, USA), and 10 wt% of polyvinylidene fluoride binder (534,000 MW, Aldrich, Allentown, PA, USA) in an agate mortar and pestle in an Ar-filled glovebox. γ-butyrolactone (99+%, Aldrich) was used as the solvent. The mixtures were dried at 80°C in an Ar atmosphere after mixing. The powder obtained was pressed at 4000 kg/cm² into ¼" diameter pellets (10-20 mg pellet weight) and was dried in an Ar-filled glovebox at 80°C for 6 hours before being assembled. All electrodes were assembled in stainless steel cells using Li foil (0.75 mm, Alfa Aesar) as the counter electrode, EC:DMC (1:1 by weight) with 1 M LiPF₆ (EM Science, Norwood, OH, USA) as the electrolyte, and Celgard™ 2400 (Celgard, Inc., Charloote, NC, USA) as the separator. Details on cell assembling are given in Chapter 2. Cycling was conducted at room temperature. All cells were tested at a 10 mA/g current rate. Except for Si, which was lithiated to 1636 mAh/g of Si (less than the theoretical maximum capacity), all samples were lithiated to maximum capacity and delithiated once before being disassembled in the glovebox. The cycled samples obtained were characterized using a Rigaku RU300 (Rigaku/MSC, The Woodlands, TX, USA) Cu-Kα radiation X-ray diffractometer (XRD), a JEOL 6320 (JEOL, Ltd., Tokyo, Japan) field emission gun scanning electron microscope (FEG-SEM), a JEOL 2010FX (JEOL, Ltd., Tokyo, Japan) high resolution electron microscope (HREM). Scanning transmission electron microscopy (STEM) was performed by Dr. Haifeng Wang, using a Fisions/ Vacuum Generators HB603 (Fiscon Instruments, VG Microscopes, East Grinstead, UK) analytical scanning transmission electron microscope.
3.3 Results and Discussion

Figure 3.1 shows a material selection map plotting the critical particle size of different lithiating metals, calculated from the Huggins-Nix model, vs. their corresponding gravimetric capacities (see Table 3.2 for values used for the calculations)\textsuperscript{13-16}. The ideal metal would lie in the upper right region of the map, having a large critical particle size (i.e. high cycling “toughness”) and a high specific capacity. Note that there is in general a trade-off between critical particle size and capacity. Due to the influence of volume strain on fracture in the model, most known lithiating metals tend to fall on the upper left or the lower right part of the map. The critical size of the materials plotted here varies, from \(~100\ \mu\text{m} \) for Se and Ga due to their high assumed toughness and small volumetric lithiated strain, to \(~1\ \text{nm} \) for Si and Ge, due to their low fracture toughness and large volumetric strain.

Figure 3.2 shows voltage profiles of the different metals during the discharge and charge process. The extent of lithiation and delithiation is also shown on the plots. Sb could be almost fully delithiated. However, only a part of the total lithium could be extracted from Al, Ag and Sn and the samples could not fully be delithiated. The residual compositions of these alloys are 0.4 molar ratio of Li/Al, 0.63 molar ratio of Li/Ag and 1.3 molar ratio of Li/Sn, respectively. Si was charged to the concentration of Li/Si molar ratio of 1.34.

Figure 3.3 shows microstructures of the metals before and after electrochemical cycling, as observed under SEM. Examination of the particles reveals fracture in both ductile and brittle metals, including Al, Sn, Sb, and Si, when the particle size is large (>5
µm). Small particles (< 0.5 µm) of Ag, however, do not exhibit cracks. These observations are generally consistent with the predictions of the Huggins-Nix model.

HREM, however, reveals more detail about the microstructures. After one full lithiation and delithiation, a highly disordered nanostructure has formed in all cases (Fig. 3.4). This nanostructure consists of crystallites of <15 nm size; in some cases (Ag and Sn) the nanocrystallites are intimately mixed with an amorphous phase. The observation of amorphous materials in these samples is a significant result and was investigated further, as presented and analyzed in Chapter 4 of this thesis. In all samples, X-ray diffraction after cycling shows peak broadening for the starting metals and Li-Me intermediate phases in the delithiated samples and lithiated samples, respectively, indicating the existence of particles less than 30 nm in size (Fig 3.5). This is consistent with the HREM observations. Across particles of 0.5-1 µm diameter, this nanostructure is uniform. Within a given particle, the transformed nanostructure shows no evidence of a common crystallographic relationship between nanocrystallites (texture). This nanostructure occurs in all of the metals observed, in metals lithiated to low capacity (LiAg) as well as to high capacity (Li13Sn5, Li5Sb). This transformation to nanocrystalline structure may occur during either the lithiation or delithiation (transformation from Me to Li-Me phase or from Li-Me phase back to Me phase).

Detailed inspection of the structural relationship between the metal and lithiated compounds has shown that the first and subsequent lithiated phases in each case have no obvious topotaxial relationship with the parent metal phase (Fig. 3.6)\textsuperscript{17-24}. This implies that the lithiated phase must form through a reconstructive, rather than a displacive, transformation; nucleation and growth must occur. In addition, the density of
nanocrystallites seen in the transformed material indicates an extremely high nuclei density of order $10^{18}$ cm$^{-3}$. These results show that transformation of the electrochemically cycled metals at room temperature results in an extremely high nucleation frequency, possibly a homogeneous nucleation process. At a larger length scale, volumetric strain can cause fracture as described above (i.e. Huggins-Nix). At a sufficiently fine particle size and low lithiation rates, however, a relatively uniform lithium concentration may form throughout the particle leading to a nanocrystalline structure without fracture.

Figure 3.7 shows the microstructure of an Sb metal anode after 50 cycles, observed in STEM. The micrograph reveals finely dispersed particles with diameters of 5-10 nm. This particle size is quite similar to the size of the nanocrystallites formed during the first lithiation cycle. The evolution of microstructure leading to failure of the electrode is summarized in Fig. 3.8.

The existence of such finely dispersed particles and their similarity to the initial nanocrystallite size lead to the following postulate: It is unlikely that fracture to such a fine length scale occurs only due to volume changes. If cracks are formed and propagated due to the volumetric strain during cycling, the resulting terminal particle size should lie in the range of the critical particle size predicted by the Huggins and Nix model. Fracture into finer particles would reduce the driving force for further crack growth. It is, therefore, likely that other mechanisms continue to propagate the cracks upon further cycling. For example, it is well known that grain boundaries or amorphous phases, having higher free energy than crystalline grains of like composition, are susceptible to preferential environmental attack\textsuperscript{25}; metal dissolution can occur in certain
environmental conditions such as in the presence of acid species from water
contamination.\textsuperscript{26,27} Stress corrosion cracking, where crack advancement is accelerated by
adsorbed chemical species reacting at the crack tip, can also occur. It is necessary to
carry out further studies before these chemical mechanisms stated can be confirmed.
However, this model could provide an explanation for the improved cyclability of those
metal oxides anodes in which the active metal is isolated from the electrolyte.

3.4 Conclusions

In lithiated metal anodes, fracture from volume changes upon lithiation occurs
large particle size ($> 1\mu m$). Due to the absence of topotaxial relationships between the
starting metal and the first lithiated phases for all of the metals tested, nanocrystalline
microstructures are created via a nucleation and growth process during the first lithiation
or delithiation. However, a direct observation of Sb cycled for 50 cycles over its entire
capacity range shows dispersed nanocrystalline particles of the same size as that which
were formed after the first cycle. This indicates a different failure mechanism for
extended cycling than proposed by many researchers. Material failure due to chemical
attack is the likely mechanism, which over multiple cycles could cause the initial
nanocrystalline composite to fracture into individual crystallites. Passivation of the
materials against chemical attack may be the key to improving the cycle performance of
metal anodes, providing even greater motivation for the development of internally
partially reduced metal-metal oxide composite anodes, as discussed in Chapter 2 of this
thesis.
3.5 References


### 3.6 Tables

**Table 3.1** Lithiating metals tested along with relevant properties.

<table>
<thead>
<tr>
<th>Metal (structure)</th>
<th>Bulk modulus (GPa)</th>
<th>1st Li-Me compound</th>
<th>Last Li-Me compound</th>
<th>$\Delta V/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (FCC)</td>
<td>103</td>
<td>LiAg</td>
<td>Li$_{10}$Ag$_3$</td>
<td>3.79</td>
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<tr>
<td>Al (FCC)</td>
<td>75</td>
<td>LiAl</td>
<td>Li$_3$Al</td>
<td>4.04</td>
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<tr>
<td>Sn (BCT)</td>
<td>58</td>
<td>Li$_2$Sn$_3$</td>
<td>Li$_{12}$Sn$_5$</td>
<td>2.59</td>
</tr>
<tr>
<td>Sb (Rhomb)</td>
<td>42</td>
<td>Li$_2$Sb</td>
<td>Li$_3$Sb</td>
<td>1.64</td>
</tr>
<tr>
<td>Si (Diamond)</td>
<td>100</td>
<td>Li$_{12}$Si$_7$</td>
<td>Li$_{21}$Si$_3$</td>
<td>2.96</td>
</tr>
</tbody>
</table>
Table 3.2  Material properties used to calculate the critical particle size in Fig 3.1

<table>
<thead>
<tr>
<th>Terminal Li Metal</th>
<th>Terminal Li Alloy</th>
<th>Number of mole of Li/metal</th>
<th>Molecular Weight of Metal (g/mole)</th>
<th>Density of Metal (g/cm$^3$)</th>
<th>Molar Volume of Metal (cm$^3$/mole of metal)</th>
<th>Molecular Weight of Terminal Alloy (g/mole)</th>
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</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Li$_{10}$Ag$_3$</td>
<td>3.33</td>
<td>107.87</td>
<td>10.5</td>
<td>10.27</td>
<td>393.01</td>
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<td>Al</td>
<td>Li$_2$Al</td>
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<td>26.98</td>
<td>2.7</td>
<td>9.99</td>
<td>74.79</td>
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<tr>
<td>Bl</td>
<td>Li$_3$Bl</td>
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<td>208.98</td>
<td>9.8</td>
<td>21.32</td>
<td>229.80</td>
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<td>B</td>
<td>Li$_8$B$_4$</td>
<td>1.25</td>
<td>10.81</td>
<td>2.34</td>
<td>4.62</td>
<td>77.95</td>
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<tr>
<td>Cd</td>
<td>LiCd</td>
<td>1</td>
<td>112.41</td>
<td>8.65</td>
<td>13.00</td>
<td>119.35</td>
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<tr>
<td>Ga</td>
<td>Li$_2$Ga</td>
<td>2</td>
<td>69.72</td>
<td>5.91</td>
<td>11.80</td>
<td>83.6</td>
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<tr>
<td>Ge</td>
<td>Li$_{122}$Ge$_5$</td>
<td>4.4</td>
<td>72.59</td>
<td>5.35</td>
<td>13.57</td>
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<td>11.34</td>
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<td>LiZn</td>
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<td>65.39</td>
<td>7.13</td>
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<td>72.32</td>
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<td>Metal</td>
<td>Density of Terminal Alloy (g/cm³)</td>
<td>Molar Volume of Terminal Alloy (cm³/mole of metal)</td>
<td>Terminal Li Compounds</td>
<td>eτ (mPa m¹/²)</td>
<td>Klc (GPa)</td>
<td>B (mm)</td>
</tr>
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<td>-------</td>
<td>---------------------------------</td>
<td>-----------------------------------------------</td>
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<tr>
<td>Ag</td>
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<tr>
<td>Bi</td>
<td>5.025</td>
<td>45.73</td>
<td>Li₃Bi 1.14</td>
<td>10</td>
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<td>6.42</td>
</tr>
<tr>
<td>B</td>
<td>1.075</td>
<td>18.13</td>
<td>Li₅B₄ 2.92</td>
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<td>320</td>
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<td>22.65</td>
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</tr>
<tr>
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<td>2.923</td>
<td>28.6</td>
<td>Li₅Ga 1.42</td>
<td>10</td>
<td>4.90</td>
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<td>48.17</td>
<td>Li₅Sb 1.64</td>
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<tr>
<td>Se</td>
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<td>Li₂Se 0.97</td>
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<tr>
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<tr>
<td>Sn</td>
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<td>Li₂₂Sn₅ 2.59</td>
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<td>58</td>
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<tr>
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<td>LiZn 0.99</td>
<td>10</td>
<td>69</td>
<td>1.42</td>
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</table>

Ref. 14 for bulk modulus of Al, In, Pb, Sn, Zn
Ref. 16 for bulk modulus of Sb, Se, Si, B
Ref. 13 for bulk modulus of Ag, Bi, Cd, Ga, Ge
Ref. 15 for Klc of Si and Ge
Klc for other elements is approximated to be ~10 mPa·m¹/²
Figure 3.1 Material selection map showing critical particle size of metals with various properties vs. specific capacity.
Figure 3.2 Voltage vs. Capacity plots of 1) Al, b)Ag, c)Sb, d)Si, and e)Sn. The values on the discharge curves indicate the number of moles of Li that alloy with the metals during the lithiation process. The number on the charge curves indicate the number of mole of Li that could be extracted out during the delithiation process.
Figure 3.3 SEM micrographs show a comparison of metal particles before and after the first cycle. Cracking was observed in metals particles of large size (>1 μm). In Ag, having a small starting particle size (< 0.5 μm), no fracture was observed.
Figure 3.4 TEM micrographs showing internal structure of cycled metals. All of them exhibit similar nanostructure consisting of nanocrystallites of less than 15 nm. The electron diffraction patterns can be indexed as the phases shown in parentheses.
Figure 3.5  XRD of  a)Ag, b)Al, c)Sb, d)Si, and e)Sn after electrochemical cycling. Notice peaks broad peaks of the metals or the lithiated compounds indicating small particle size.
Figure 3.6  Structures of tested metals along with that of their first Li-Me compound.13-20
**Figure 3.7** Dispersed nanocrystalline particles of Sb with ~5 nm in size are found after extensive cycling. (STEM by Dr. H. Wang)

**Figure 3.8** Schematic illustrating the evolution of metal microstructures. After one lithiation cycle, fracture occurs in particles of large size (>1μm). Lithiation causes nanocrystallites of less than 15 nm in size to form via a nucleation and growth process. After extensive cycling, these nanocrystallites are dispersed.
Chapter 4

Electrochemically-Induced Solid-State Amorphization

4.1 Introduction

In Chapter 3, TEM studies of electrochemically cycled Li-Me anode materials in the delithiated or partially delithiated state revealed some degree of disordering. As an understanding of the evolution of microstructure during lithium alloying and dealloying is crucial to the design of rechargeable battery anodes, we present in this Chapter an investigation of this process, using HREM and calibrated XRD. A thermodynamic and kinetic rationale leading to identification of a new phenomenon, electrochemically-induced solid-state amorphization, is presented to explain microstructural observations. In addition, results are discussed in the context of subsequent nanocrystallite formation upon electrochemical cycling, and potential failure mechanisms.

4.2 Background (Solid-State Amorphization)

Nearly 20 years ago, formation of amorphous materials, by a solid-state reaction rather than from the melt, was observed in multilayered thin films. The phenomenon is now known as solid-state amorphization (SSA). Solid-state amorphization occurs
through diffusive reactions in multilayer films where the film thickness is comparable to interfacial thickness.\(^1\) It has been explained as the formation of a glassy phase that is metastable, yet lower in free energy than the pure reactant phases, occurring when a thermodynamically preferred crystalline intermediate phase is unable to crystallize. SSA has similarities to earlier-observed reactive glass formation between bulk crystalline oxides such as SiO\(_2\)-Al\(_2\)O\(_3\); both have been described in phase-diagram terms as metastable extensions of the liquidus curves to temperatures below the glass transition temperature (\(T_g\)) of the resulting liquid compositions. Reactions taking place below \(T_g\), therefore, form a glass at rates determined primarily by solid-state interdiffusion\(^3\). It has been found that typical characteristics of a system that can transform from a crystalline to an amorphous phase via a solid-state amorphization reaction are\(^1,3-9\):

1) negative heats of mixing  
2) large differences in atom size;  
3) high alloying concentrations; and  
4) large differences in the atom diffusivities

Negative heat of mixing provides the driving force for alloying or compound formation reactions between the starting phases. Large size differences between atoms, high alloying concentration, and large differences in the atom diffusivities tend to result in a large nucleation barrier and instability of the daughter crystalline phase. Avoidance of nucleation of the intermediate crystalline phases allows solid-state amorphization to occur. Some might consider externally driven processes such as ion mixing by implantation and mechanical-alloying to also be solid-state amorphization processes.
However, these kinds of processes are not included here as they require external energy inputs.

Thin-film solid-state amorphization has not previously been studied in any Li-Me alloy. However, these alloys do exhibit many of the characteristics, discussed above, that are typically associated with metallic glasses formed by solid-state reaction. There have been recent reports in the literature of disorder in electrochemically-lithiated metals and metalloids, observed with X-ray diffraction or high resolution microscopy in Al thin films\textsuperscript{10} and Si nanowire or nanoparticle systems\textsuperscript{11,12}. However, while these observations have suggested that disordering can occur in Li-Me systems, no detailed mechanism has been discussed. In the case of the nanoscale systems\textsuperscript{11,12}, it has been argued that the disorder is a size effect. No evidence for amorphization of bulk Li-Me alloys has been provided. In this work, we present evidence of electrochemically-induced solid-state amorphization reactions in bulk and thin film metals using calibrated X-ray diffraction, and HREM direct observations.

4.3 Experimental Procedure

4.3.1 Powder Experiments

Various Li-Me alloys including Li-Sn, Li-Ag, Li-Al and Li-Si were investigated. Li-Si was chosen as a model system, and received more extensive analysis, because its phase equilibria are well-established\textsuperscript{13}, amorphous silicon is structurally well-understood, and it is one of the leading candidates for future lithium battery anodes. The Li-Si phase diagram (Fig. 4.1) exhibits numerous intermetallic phases, the nucleation and growth of which must be avoided if solid-state amorphization is to occur. The fact that the
intermediate compounds have complex crystal structures\textsuperscript{14} with little structural similarity to the pure endmembers was expected to help frustrate crystallization, since continuous transformation of, or epitaxial growth on, the parent phases is unlikely. Note that while electrochemical measurements have been used to establish the phase relations in Li-Si as well as other Li-Me alloy systems these have been conducted under conditions (low current rates, elevated temperatures) that promote the formation of the equilibrium crystalline phases.\textsuperscript{13}

XRD and HREM experiments were performed on powder samples of Ag (0.5-1 μm, 99.9% Alfa Aesar, Ward Hill, MA, USA), Al (-325 mesh, 99.5% Alfa Aesar), Sn (-325 mesh, 99.8% Alfa Aesar) and Si (-325 mesh, 99.5% Alfa Aesar). The as-received metal powders were used to make pellets for electrochemical testing. In order to quantify the amount of crystalline silicon phase throughout the electrochemically-induced transformation, either fine nickel powder (0.08-0.15 μm, 99.8% Alfa Aesar) or fine copper powder (0.2-0.3 μm, 99.9% Alfa Aesar) was added as a non-reactive internal standard to the starting metal powder. (It is possible that solid-state amorphization has been overlooked in previous experiments using X-ray diffraction as a characterization tool, due to the absence of internal standards allowing the amount of crystalline phase to be quantified.) The tested electrodes were prepared by mixing internal standard Ni or Cu powder with the metal powder and polyvinylidene fluoride binder, PVDF (534,000 MW, Aldrich, Allentown, PA, USA). The weight ratio of the three components is shown in Table 4.1. Mixing was done using an agate mortar and pestle in an Ar-filled glovebox with less than 3 ppm oxygen and H\textsubscript{2}O. γ-butyrolactone (99+%, Aldrich) was used as the solvent. The mixtures were dried, made into pellets and assembled into electrochemical
cells using the same procedure as described in Chapter 3. The metal pellets were tested as the positive electrode against Li foil (0.75 mm thick, Alfa Aesar) using Celgard 2400™ as the separator. The electrolyte used was a 1 M solution of LiPF₆ in a 1:1 mixture (by weight) of ethylene carbonate, EC, and dimethyl carbonate, DMC, (EM Science, Norwood, OH, USA). The electrochemical tests were carried out at room temperature at a current density of 10 mA/g of active material.

The reference powders with known amounts of each crystalline phase were prepared for XRD by mixing dry powder of each of the components shown in Table 4.1. X-ray diffraction was performed before and after lithiation, using a Rigaku diffractometer (Rigaku, RU300, continuous scan with 0.75° scan speed, 0.02° interval, 1° divergence and scatter slits and 0.03° receiving slit with Cu-Kα radiation). The lithiated samples were prepared for XRD by disassembling the electrochemical cells in an Ar-filled glovebox and placing the active material on an X-ray holder on a glass slide with double-sided tape (3M, St. Paul, MN, USA). The sample holders were then sealed with Kapton™ tape (VWR Scientific, West Chester, PA, USA) in order to avoid possible reaction of samples with the atmosphere during the XRD. XRD results of the lithiated samples were compared with the patterns from unlithiated reference samples. The relative amounts of crystalline phases were quantified using the method described in Cullity. Example calculations can be found in detail in Appendix B.

High resolution and analytical electron microscopy experiments were performed using a JEOL 2010FX TEM (JEOL, Ltd., Tokyo, Japan) operating at 200 keV and equipped with an energy-dispersive X-ray detector (Link Systems, Oxford Instrument, High Wycombe England, UK). The lithiated positive electrodes were prepared by
dispersing a small piece of the pellet in $\gamma$-butyroactone (534,000 MW, Aldrich) using an ultrasonicator. The dispersed powder solution was then dropped onto a nickel or copper grid coated with a carbon film or lacy carbon coated formvar film (EM Microscopy Science, Fort Washington, PA, USA), and dried in an Ar-filled glovebox. The samples were loaded into the TEM specimen holder while in the glovebox. The specimen holders were then transported to the TEM in a sealed container, and loaded into the instrument with less than 30s exposure to air.

4.3.2 Thin Film Experiments

As discussed earlier, the systems studied also meet the requirements for thin film solid-state amorphization. To make a direct comparison to reactions involving a conventional thin film geometry, experiments were carried out on the Li-Sn and Li-Si systems. These were done in collaboration with Dr. Young-Il Jang at Solid State Division, Oak Ridge National Lab, Oak Ridge, TN, USA.

Si films of 0.5 $\mu$m thickness were deposited on polycrystalline Al$_2$O$_3$ plates by direct current (dc) magnetron sputtering of a Si target (Kurt J. Lesker, 99.999%) in Ar atmosphere. The films were annealed at 1000°C for 10 h in Ar. Li films of 1.5 $\mu$m were deposited on the Si films by thermal vapor deposition of Li metal to obtain a Li/Si molar composition ratio of 2.816.

Sn was deposited on an Al$_2$O$_3$ substrate to a thickness of 0.3 $\mu$m. The film was confirmed to be crystalline Sn before the next step of Li deposition was continued. Li film was deposited on top of the Sn thin film to obtain a Li/Sn molar composition ratio of 4.4 mole (1.06 $\mu$m).
All films were packaged by a layer of lithium phosphorous oxynitride (Lipon)\textsuperscript{16} of 0.2 μm thickness, obtained by radio frequency (rf) magnetron sputtering of Li\textsubscript{3}PO\textsubscript{4} in N\textsubscript{2} atmosphere. Between the Li and Lipon depositions, the samples were handled in a glove box filled with Ar. The samples were characterized by XRD using Cu K-α radiation. All procedures were carried out at room temperature.

4.4 Results and Discussion

4.4.1 Li-Si System

4.4.1.1 Electrochemical and Microstructural Characterization

The Si powder sample was lithiated to a total capacity of 1283 mAh/g (Li/Si molar ratio of 1.34 or 57 mole% Li). The voltage profile is shown in Fig. 4.2, showing a flat voltage plateau at 0.1 V. Note that this voltage profile does not follow that corresponding to the formation of the equilibrium crystalline phases where a new voltage plateau is observed in each two-phase field of constant lithium chemical potential (Fig. 4.3). Over the composition range of the electrochemically-lithiated sample, two-phase coexistence of the equilibrium crystalline phases Si and Li\textsubscript{12}Si\textsubscript{7}, with a voltage plateau of ~0.34 V, is expected, Fig 4.3.\textsuperscript{13} The lower voltage of 0.1 V indicates a significant deviation from equilibrium phase formation.

Figures 4.4a and 4.4c compares X-ray diffractograms of the Ni and Si powder mixture before and after lithiation. If equilibrium were maintained along this composition trajectory, Li\textsubscript{12}Si\textsubscript{7} should crystallize and increase in relative fraction while coexisting with crystalline Si. Figure 4.4c does show a decrease in the Si phase reflections relative to the Ni reference, from which it was determined that 38 weight % of
the starting silicon phase remained. However, no new reflections showing formation of any crystalline phase appeared. From the remaining crystalline Si fraction, determined from the Ni-calibrated XRD (Fig. 4.4c), and the total lithium transported (Fig. 4.2), the Li/Si molar ratio of the amorphized reaction product was calculated to be 2.17 (68 mole% Li). This composition is shown as the terminal composition along the trajectory in Fig. 4.1. The uniformity of composition amongst those particles showing solid-state amorphization cannot be determined at present since the Li concentration in individual particles has not been characterized.

High resolution and analytical electron microscopy was conducted on the lithiated positive electrode, and showed results consistent with the XRD results. The sample microstructure was found to be dominated by amorphous phase particles, the composition of which was shown via energy-dispersive X-ray analysis (EDX) to be Si-rich. Figure 4.5 shows the HREM bright field images, corresponding dark field images, a selected-area diffraction pattern, and an energy-dispersive spectrum of typical amorphous particles. The images and electron diffraction pattern show the disorder and diffuse rings, respectively, that are characteristic of a glass. The dark field image formed by using the diffracted intensity from the first diffuse ring, as shown in Fig. 4.5b, shows homogeneous scattering intensity and no sign of strongly diffracting regions larger than a few angstroms, confirming the absence of crystalline phases. The EDX spectrum shows predominantly Si; Li is not detectable with the detector used. The low oxygen concentration shows that this is not an oxidized amorphous silicon oxide particle. The majority of the particles analyzed by HREM were of this type. Crystalline Si particles
were also observed, consistent with the XRD results. In some cases a coexistence of amorphous phase and crystalline Si were observed in the same particle.

The structure of the electrochemically-driven solid-state amorphization product can be compared to that of amorphous Si produced by vapor-deposition and annealing in the classical study by Moss, et. al\textsuperscript{17}. The present data was analyzed by taking the scattered intensity of the electron diffraction pattern as a function of scattering vector, \( k \). Electron diffraction patterns taken from various lithiated silicon particles were analyzed using SEMPER\textsuperscript{TM} software (Synoptics Ltd., Cambridge, England) and were plotted against that of the vapor-deposited amorphous Si film in Fig 4.6. Within the experimental error, determined by the contrast in the diffraction pattern and the spatial resolution of the analysis software, the analyzed intensities as a function of \( k \)-vector of several lithiated Si particles were found to be the same as that of the vapor-deposited amorphous Si film, having broad peaks at \( k \)-vector \( \sim 2.0 \text{ Å}^{-1} \) and at \( \sim 3.6 \text{ Å}^{-1} \).

Note that since the scattered intensity is proportional to the square of its atomic scattering factor,\textsuperscript{15} the contribution of Li atoms to the scattered intensity is in this case more than an order of magnitude less than that of Si. The scattered intensity observed is, therefore, probably mainly due to Si atoms. The close correspondence of diffraction peaks in Fig. 4.6 indicates similar atomic arrangements of Si network in the lithiated Si to that of the conventional amorphous Si. The atomic arrangement in conventional amorphous Si has been used as the exemplar of a tetrahedrally boned continuous-random network glass.\textsuperscript{18} The present data, therefore, suggest that the structure of amorphous Li-Si consists of a continuous-random network of Si tetrahedra, into which Li atoms are inserted. This structure differs significantly from that of the expected
crystalline phase, Li$_{12}$Si$_7$ (Fig 4.7)\textsuperscript{19} at which planar Si$_5$ rings are accompanied by planar Si$_4$ stars and Li atoms to form an extended orthorhombic crystal structure.

4.4.1.2 Thermodynamic Interpretation

To understand why electrochemically-induced solid-state amorphization would occur in Li-Me systems, it is worthwhile to consider the different possibilities as Li is driven to the metal electrode. Figure 4.8 shows 4 different cases. In case I, lithium metal may simply be electroplated; this would be the case if Li$^+$ is driven at a very high rate so that it cannot diffuse into the metal or if the metal does not alloy with Li. This does not happen in our experiment as no lithium metal plating was observed on the samples tested. In case II, electrochemically-driven supersaturation of the alloy might occur via an "implantation" mechanism. This situation is highly unlikely for the present materials since a conductive metal electrode cannot support an appreciable internal electric field. While for a metal there is no apparent driving force for this mechanism under the conditions used, supersaturation may be possible in less conductive compounds such as transition metal oxides. Case III is a conventional alloying situation in which the system forms solid solutions or crystalline compounds in accordance with the equilibrium phase diagram. This option is expected to occur at a rate limited by Li diffusion as in a binary diffusion couple. However, if the expected Li-Me crystalline phase formation is not kinetically permitted, and amorphous phase formation is thermodynamically allowed (meaning the total Gibbs-free energy change is negative), the fourth option, case IV, a solid-state amorphization reaction would instead occur.
As our experimental data has shown, the Li-Si system follows the fourth option in forming an amorphous Li-Si phase. Using thermodynamic data from the literature for Li, Si and the equilibrium crystalline Li-Si compounds (Table 4.2),\textsuperscript{20,21} coupled with data obtained from electrochemical testing for the amorphous Li-Si formed, we were able to construct a Gibbs-free energy diagram for the crystalline and amorphous phases in this system, shown in Fig. 4.9. The following procedure was followed in constructing the Gibbs energy diagram.

1) The equilibrium Li-Si crystalline phases were treated as line compounds. The values on the free energy diagram for Li\textsubscript{i}Si\textsubscript{y} were calculated as in the following example.

\[
12 \text{Li} + 7 \text{Si} \rightarrow \text{Li}_{12}\text{Si}_{7} \quad (4.1)
\]

The standard free energy of reaction in Eq. 4.1

\[
\Delta G_{\text{Li}_{12}\text{Si}_{7}}^o = G_{\text{Li}_{12}\text{Si}_{7}}^o - 12G_{\text{Li}}^o - 7G_{\text{Si}}^o \quad (4.2)
\]

where \(G_i^o\) is the standard free energy of \(i\) obtained from Ref. 20 and 21(Table 4.2). Since temperature dependence of the free energy of Li-Si alloys was not available and this dependence would likely change the free energy values by less than one percent, for these calculations it was assumed that the free energy values at room temperature do not deviate from the values reported at 415\(^\circ\)C. The values for pure Li and Si are the values at 25\(^\circ\)C.

\[
\Delta G_{\text{Li}_{0.37}\text{Si}_{0.63}}^o, \text{the free energy of formation per mole of the binary system of composition X}_{\text{Si}} = 0.37, \text{was then calculated from}
\]

\[
\Delta G_{\text{Li}_{0.37}\text{Si}_{0.63}}^o = \frac{\Delta G_{\text{Li}_{12}\text{Si}_{7}}^o}{12 + 7} \quad (4.3)
\]
At 415°C (688 K), the Nernst equation

\[ \Delta G^o_{Li_{0.65}Si_{0.35}} = -nFV \]  \hspace{1cm} (4.4)

where \( V \) = Voltage relative to Li metal (from voltage plateau from the electrochemical result)

\( F \) = Faraday constant = 23.060 kcal/V mole

\( n \) = number of charges transported in the reaction (= 1)

gives the voltage of the first plateau in Fig. 4.3 at 0.33 V (n=0.63).

2) The composition of the amorphous Li-Si phase was assumed to be the average composition of lithiated Si calculated from the calibrated XRD experiment (68 mole% Li, LiSi_{0.47}). The reaction can be written as:

\[ \text{Li} + 0.47 \text{Si} \longrightarrow \text{LiSi}_{0.47} \]  \hspace{1cm} (4.5)

\( \Delta G^o_{LiSi_{0.47}} \), the free energy of formation of the amorphous Li-Si was then calculated from the voltage profile obtained (Fig. 4.2) using the Nernst equation to be -2.306 kcal/mol. Note that polarization of the sample was assumed to be negligible; the voltage obtained from the electrochemical testing was treated as an equilibrium voltage corresponding to the amorphous Li-Si and Si two-phase field.

\( \Delta G^o_{Li_{0.40}Si_{0.32}} \), the standard free energy of formation per mole of the binary system of composition \( X_{Si} = 0.32 \) could then be calculated from

\[ \Delta G^o_{Li_{0.40}Si_{0.32}} = \frac{\Delta G^o_{LiSi_{0.47}}}{1 + 0.47} \]  \hspace{1cm} (4.6)

The free energy curve of the Li-Si amorphous phase, except at the composition of 68 mole% Li, is schematically drawn in Fig. 4.9.
The free energy construction (Fig. 4.9) is consistent in every aspect with the experimental data obtained:

- As the lithium concentration increases, crystalline Si and amorphous Li-Si phase coexist. During the electrochemical testing, a long plateau at about 0.1 V was observed, indicating the existence of a two-phase equilibrium.
- The XRD result confirms that only one crystalline phase, Si, is present.
- The HREM result shows the existence of a crystalline Si and amorphous Si containing phase.

The coexistence of a crystalline phase and amorphous phase produced by SSA has also been observed in the Au-La thin film system.¹

### 4.4.1.3 Effect of Higher Lithiation

Another experiment was conducted in which three crystalline phases would have been expected to form if equilibrium was maintained. A Si sample was electrochemically lithiated to a higher lithium concentration, corresponding to a total capacity of 2166 mAh/g (Li/Si molar ratio of 2.26 or 69 mole% Li) before reaching the terminating voltage of 0.005 V. Figure 4.10 shows the corresponding voltage profile, having a nearly flat voltage plateau ending at around 0.09 V, similar to that of the Li-Si sample lithiated to a lower lithium concentration. This voltage profile, as mentioned before, indicates a deviation from equilibrium phase formation. Figures 4.4a and 4.4b compares X-ray diffractograms of the Ni and Si mixture before and after lithiation. The amount of remaining crystalline Si was less in this sample than in the previous sample, as expected from the higher lithiation. The decrease in the integrated peak intensities for Si phase

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reflections, relative to those for the Ni reference, was analyzed and showed that 10 mole% of the starting silicon phase remained. The amorphous Li-Si reaction product was calculated to have a terminal Li/Si molar ratio of 2.82 (74 mole% of Li). This concentration is shown as the endpoint of the trajectory in Fig. 4.11. If thermodynamic equilibrium were obtained, Li$_{12}$Si$_7$ phase is expected to first form, and as the Li concentration increases to the end composition of the trajectory, the Li$_{12}$Si$_7$ phase would disappear while the new crystalline phases Li$_7$Si$_3$ and Li$_{13}$Si$_4$ would form. However, the XRD pattern does not show any of the expected Li-Si crystalline peaks. Small unidentified broad peaks at 2θ = 39.42°, 41.26° and 43.08°, corresponding to d-spacings of 2.28 Å, 2.19 Å, and 2.10 Å, were instead detected.

The HREM shows the sample to consist of amorphous phase particles (Fig. 4.12). Diffuse rings at the same position as in the previous sample were observed. The sample also shows the existence of nanocrystalline particles. In some particles, amorphous phase coexisting with nanocrystallites were observed (Fig. 4.13). The composition of these particles was shown via energy-dispersive X-ray analysis (EDX) to also be Si-rich.

The existence of the broad, unidentified XRD peaks accompanied by the HREM results suggested that a Li-Si metastable crystalline phase coexists with Li-Si amorphous phase in Si lithiated to higher concentrations. Since the observation by HREM reveals that the majority of particles are amorphous, the composition of this Li-Si metastable crystalline phase field is expected to be at a composition higher than 74 mole% Li, the average composition of the sample. In order to get the exact composition of this phase, the relative volume fraction of the crystalline and amorphous phases must be known. However, this information is not available. To illustrate a likely Gibbs free energy
construction, it is assumed that 1/4 of the sample exists in the metastable Li-Si crystalline form. The resulting Gibbs free energy diagram, shown in Fig. 4.14, illustrates that two metastable phases, one crystalline, one amorphous, can coexist in the sample at this composition.

4.4.1.4 Thin-Film Solid-State Amorphization Experiment

A Li-Si thin-film solid-state amorphization experiment was conducted by Dr. Young-II Jang at Oak Ridge National Laboratory (Oak Ridge, TN) as described in 4.3.2. A 1.5 μm Li film was evaporated onto a Si film with the thickness 0.5 μm, yielding a Li/Si molar ratio of 2.815. XRD results of the Si film before and after Li film deposition are shown in Fig. 4.13. A significant reduction in Si peak intensity is observed, indicating that reaction of Li with Si occurs upon deposition and at room temperature. However, consistent with the electrochemically lithiated Si experiment, none of the expected Li-Si intermediate crystalline phases were found. This supports the hypothesis that the reaction that occurs under electrochemical insertion can also occur in a conventional solid-state amorphization reaction at room temperature.

4.4.2. Other Systems

In addition to the model system Li-Si, three other Li-Me systems have been investigated. As discussed in the following section, some show amorphization upon electrochemical lithiation and some do not.
4.4.2.1 Li-Sn System

It was found in the Li-Sn system that none of the expected Li-Sn crystalline phases formed upon lithiation to 75 mole% Li. Similarities between Sn powder subjected to electrochemical insertion and a bilayer solid-state reaction between Li and Sn thin films were found. The same reaction product was observed in both experiments. This supports the model proposed that the same metastable products can be induced by electrochemical lithiation as in other solid-state reactions.

Electrochemical lithiation experiments were performed on Sn powder samples. A Sn sample was lithiated in the same manner as the sample in section 4.4.1.1, until it reached a lower voltage limit of 0.005 V (Fig 4.16a). This cell had a discharge capacity of 672 mAh/g (Li/Sn molar ratio of 2.98 or 75 mole% Li) as shown in Fig. 4.17.

Following the trajectory shown in Fig. 4.17, six new equilibrium crystalline Li-Sn phases would be expected to form with increasing lithiation, ending with $\text{Li}_{13}\text{Sn}_5$-$\text{Li}_7\text{Sn}_2$ as the sample reaches the end composition (75 mole% Li). In contrast to the 0.660 V (0.4-0.7 Li/Sn molar ratio), 0.530 V (0.7-2.33 Li/Sn molar ratio), 0.485 V (2.33-2.63 Li/Sn molar ratio), and 0.420 V (2.6-3.5 Li/Sn molar ratio) voltage plateaus expected for Sn lithiated to this composition (Fig. 4.18), Fig. 4.14a shows a single voltage plateau at $\sim 0.36$ V with a long sloping profile. This deviation from the equilibrium voltage profile indicates a different phase formation process than the equilibrium $\text{Li}_{13}\text{Sn}_5$ and $\text{Li}_7\text{Sn}_2$ phases expected. The XRD result shows that all Sn particles were reacted since no remaining peaks of Sn could be observed (Fig 4.19c). None of the expected peaks for Li-Sn crystalline phases were seen; only broad low intensity peaks at $2\theta = 38.58^\circ$, 55.96$^\circ$ and 69.52$^\circ$ were found. These unidentified peaks could be translated to d-spacings of 2.33 Å,
1.64 Å and 1.35 Å, respectively. In addition, these peaks are similar to those observed by Dahn, et. al.\textsuperscript{23} in SnO in which it is first electrochemically reduced to Sn metal before being lithiated to a composition of 2.5-4.4 Li/Sn molar ratio (71.4 – 81.5 mole% Li). According to Dahn et. al, these broad, low intensity peaks arise from randomly arranged Sn-tetrahedra on an underlying BCC lattice.

To see whether these peaks only appear when Sn is lithiated to a high lithium concentration, another Sn sample was discharged to the average composition of the first Li-Sn compound, Li\textsubscript{2}Sn\textsubscript{5}, (90.32 mAh/g or 28.6 mole% Li). The resulting voltage profile is shown in Fig. 4.16b. The XRD diffraction pattern of the lithiated Sn sample shows a small amount of unreacted Sn. The small broad peak at $\theta = 38.58^\circ$ found upon lithiating Sn to 75 mole% Li was also observed in this sample (Fig. 4.19b). However, the peak appears to have a much lower peak intensity. This result suggests that a similar ordering of Sn tetrahedra that formed in the sample lithiated to high Li concentration started at an early stage of lithiation (assuming homogeneous lithiation). As Li concentration increases, the amount of this metastable phase increases.

A bilayer consisting of a Li film deposited on top of a crystalline Sn film was prepared and analyzed by Dr. Young-Il Jang (Oak Ridge National Laboratory, Oak Ridge, TN) as described in section 4.3.2. The Li/Sn molar ratio of the combined bilayer was 4.4. As in the Li-Si case, the two films reacted upon deposition without further heat treatment. The XRD patterns of the sample before and after Li film deposition are shown in Fig. 4.20. The XRD data obtained from the bilayer experiment show many similarities to the data from the electrochemically-lithiated Sn powder experiments (Fig. 4.19 vs. Fig 4.20). The thin film solid-state reaction sample also does not show any XRD peaks.
corresponding to the expected Li-Sn crystalline phases. Broad low intensity peaks at the same position as those found in the electrochemically lithiated Sn powder samples were observed. By calibrating the integrated XRD intensity of the Sn peaks after the Li deposition with the Al₂O₃ peak, it was found that approximately 10 mole % of Sn remained unreacted. Assuming that all Li was reacted, the composition of the lithiated Sn was determined to be 83 mole% Li (4.89 Li/Sn molar ratio). Attempts were made to observe, by HREM, the lithiated Sn powder and thin film samples. However, due to the large particle size of the powder samples and sample instability under the electron beam in the case of the thin film sample, clear results were not obtained. However, these results again show that the reaction that a metastable phase formed by electrochemical insertion also forms in a solid-state thin film reaction.

4.4.2.2 Li-Ag System

Ag powder was lithiated to a total capacity of 277 mAh/g (Li/Ag molar ratio of 1.11 or 53 mole% Li) before reaching the cutoff voltage of 0.005 V. The sample exhibited a voltage plateau at ~1.25 V and 1.5 V in the early stage of lithiation (< 65 mAh/g), followed by a long lower voltage plateau at ~0.08 V (Fig. 4.21). The voltage plateaus at high voltage are probably due to the oxidation of Ag particles leading to electrochemical reduction reaction of Ag-oxide to Ag metal by Li⁺. The lower voltage plateau at ~0.08 V corresponds to the alloying of Li with Ag metal. The composition of the lithiated Ag metal, accounting for oxidation, could be recalculated to be 45 mole% Li (Li/Ag molar ratio of 0.85) as shown along the trajectory in Fig 4.22.⁴
Figure 4.23 compares calibrated XRD patterns of Ag samples before and after lithiation. The above electrochemical results and the Li-Ag phase diagram (Fig. 4.22) suggest that the majority phase should be $\alpha$-Ag solid solution crystalline phase. The presence of this phase would be indicated by broad or shifted peaks at the location of the starting Ag peaks in the XRD pattern. From the integrated peak intensity in the XRD spectrum, however, it was found that only a small amount (~3%) of the total Ag is present in the Ag phase or its solid solution. The majority of the crystalline phase found by XRD was LiAg. Further analysis of the integrated peak intensities of each crystalline phase revealed that only 52% of the starting amount of Ag could be accounted for by the sum of crystalline phases (Ag and LiAg) after lithiation. Therefore, it is concluded that parts of the lithiated Ag must exist in a non-crystalline form. The formation of LiAg instead of the solid solution phase shown in the equilibrium phase diagram suggests that the lithiation in this sample is inhomogenous; the transformation of Ag to crystalline LiAg must occur on a particle to particle basis (dependent upon particle morphology/defect characteristics).

Inspection of the sample using HREM 13 days after lithiation revealed no amorphous Ag containing phase. A second XRD scan showed that the sample had altered upon storage in an Ar-filled glovebox (13 days at room temperature) between lithiation and subsequent XRD and HREM characterization. Comparisons of XRD patterns of the lithiated Ag sample immediately after lithiation, and after 13 days of storage at room temperature in an Ar atmosphere, are shown in Appendix C. XRD of the sample after storage showed a decrease in LiAg intensity for LiAg peaks at $2\theta = 28.18^\circ$, $40.23^\circ$ and $49.79^\circ$. In addition, higher intensity Ag peaks were observed along with a
new peak at 39.46°. This suggests that crystallization of Ag might have occurred during storage, and other metastable crystalline phases might have formed, producing the nanocrystallites observed in HREM, at the expense of any amorphous material formed upon lithiation.

4.4.2.3 Li-Al System

The Li-Al system was selected for the lithiation experiments for comparison with previous lithiation experiments performed on (111) Al thin films by Hamon, et al.10, in which formation of an amorphous LiAl phase was hypothesized. Al powder was lithiated to the maximum lithiated concentration of 921 mAh/g (Li/Al molar ratio of 0.927 or 48 mole% Li) before reaching the cutoff voltage of 0.05 V. The voltage profile shows a plateau at ~0.25 V which is slightly lower than the 0.36 V, the equilibrium voltage of the LiAl phase (Fig. 4.24).25 This is probably due to polarization of the sample. The extent of lithiation is shown on the LiAl phase diagram26 in Fig. 4.25. Calibrated XRD experiments showed that a significant amount of equilibrium crystalline LiAl was detected, accompanied by a small amount of unreacted Al. By comparing the integrated intensity of the Al-containing phase before and after lithiation with the Cu reference peaks, it was found that the total amount of Al existing in crystalline phases was > 85 % of that in of the starting amount of Al (Fig 4.26). This, therefore, shows that most of the Al exists in a crystalline form. Li-Al system is an example system in which electrochemically-induced solid-state amorphization does not occur extensively, under these experimental conditions. This is probably due to the simple NaTI structure (Fig. 4.27)26 of the Li-Al crystalline compound that is more easily nucleated.
This observation differs from the result obtained in an electrochemically lithiated Al thin film by Hamon, et. al \(^{10}\). In their experiment, no LiAl compound formation was observed in XRD, and thus it was hypothesized that an amorphous phase was formed. In light of the new results presented here, Hamon’s results could perhaps be interpreted in the following way. First, the formation of a nanocrystalline LiAl structure would be indicated by the presence of broad peaks in an XRD result. Considering that the intensity of the textured Al peak in their starting material was significantly smaller than that of the substrate, one would expect that a broader nanocrystalline peak with the same integrated intensity (and thus lower maximum intensity) would be fairly imperceptible, perhaps giving the impression of formation of an amorphous phase. Second, if more direct observation of the lithiated Al thin film were to reveal an amorphous phase, it must be noted that the rate of lithium insertion in the experiments reported in this thesis was an order of magnitude lower than theirs, thus providing more time for crystallization of the equilibrium phase.

4.5 Conclusions

In this work, experimental observations via calibrated XRD and HREM have revealed that formation of metastable non-crystalline phases can readily occur at room temperature in various pure metal systems subjected to electrochemical lithiation. This phenomenon has been described as a new type of solid-state amorphization—

\textit{electrochemically-induced solid-state amorphization}, during which a metal is amorphized upon alloying with Li during electrochemical cycling. The Li-Si alloy system was used to investigate the proposed phenomenon, combining the direct and indirect observations
of microstructure with the techniques mentioned above, with data obtained from electrochemical experiments. The electrochemical data obtained showed that equilibrium voltage steps corresponding to the Li-Si equilibrium phase formation did not occur, suggesting the formation of a metastable phase during lithiation. XRD performed on Si lithiated to a Li concentration of less than 68 mole% Li also showed no evidence of any Li-Si crystalline phase formation. In addition, a highly disordered structure, consisting predominantly of Si (in Li-Si samples) observed under HREM (direct imaging and diffraction) provided further evidence of amorphous phase formation. Furthermore, analysis of the diffraction patterns obtained under HREM revealed structural similarities between the lithiated Si phase and conventional amorphous Si.

Similar trends were observed in Si lithiated to 75 mole% Li, and in Sn lithiated to 28-75 mole% Li. In the first case, the amorphous phase was found to coexist with a minor amount of metastable crystalline phase. In the second case, a metastable crystalline phase was found to form as well. Supporting bilayer-thin film solid-state reaction experiments in Li/Si and Li/Sn showed similar results to their bulk Li-Si and Li-Sn counterparts. In the case of lithiated Ag, XRD results suggested that a large amount of Ag existed in an amorphous form immediately following lithiation, but room temperature crystallization of the sample prohibited direct observation of this phase via HREM. Lithiated Al did not appear to show significant amorphization, which was perhaps due to the simple crystal structure of the lithiated phase LiAl allowing nucleation. The results differ from literature results on electrochemically lithiated (111) Al thin films. A thermodynamic analysis and rationale was also presented to explain the occurrence of electrochemically-induced solid-state amorphization.
The results obtained from this chapter could further explain the microstructural evolution of electrochemically cycled metals found in Chapter 3. At low temperature and high current rate, as crystalline metals are subjected to electrochemical lithiation, amorphous or metastable nanocrystalline phases form. As the alloy is delithiated, the pure metal nucleates from the highly disordered phases, producing the nanocrystallites observed in Chapter 3. The absence of any topotaxial relationship between parent and daughter crystalline phases due to lithiation supports the hypothesis that nucleation and growth occurs must occur from an amorphous phase. The evidence of nucleation of the crystalline phase from an amorphous or partially disordered phase is further supported by the non-textured nanocrystalline structure found in electrochemically-cycled metals as shown in Fig 3.4.
4.6 References


4.7 Tables

Table 4.1 Weight ratios of lithiating metal, reference powder (Ni or Cu) and binder (PVDF) for calibrated X-ray diffraction experiments.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Lithiating Metal: Reference:Binder</th>
<th>Weight Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Si:Ni:PVDF</td>
<td>60:30:10</td>
</tr>
<tr>
<td>Sn</td>
<td>Sn:Ni:PVDF</td>
<td>40:50:10</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag:Cu:PVDF</td>
<td>40:50:10</td>
</tr>
<tr>
<td>Al</td>
<td>Al:Cu:PVDF</td>
<td>70:20:10</td>
</tr>
</tbody>
</table>

Table 4.2 Standard Gibbs free energies of Li at 25°C\textsuperscript{20}, Si at 25°C\textsuperscript{20} and Li-Si Alloys at 415°C\textsuperscript{21}.

<table>
<thead>
<tr>
<th>Phases</th>
<th>G\textsubscript{i} (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>-2.072</td>
</tr>
<tr>
<td>Li\textsubscript{12}Si\textsubscript{7}</td>
<td>-199.516</td>
</tr>
<tr>
<td>Li\textsubscript{7}Si\textsubscript{3}</td>
<td>-109.944</td>
</tr>
<tr>
<td>Li\textsubscript{13}Si\textsubscript{4}</td>
<td>-183.956</td>
</tr>
<tr>
<td>Li\textsubscript{22}Si\textsubscript{5}</td>
<td>-273.375</td>
</tr>
<tr>
<td>Si</td>
<td>-1.341</td>
</tr>
</tbody>
</table>
Figure 4.1 Li-Si phase diagram showing numerous intermediate phases. The trajectory shown corresponds to the composition of the electrochemically lithiated Si shown in Fig. 4.2.
Figure 4.2 Voltage profile of Si sample lithiated to 1283 mAh/g of total Si (1.34 mole Li/mole of total Si, 57 mole% Li/total Si). The flat voltage plateau at ~0.1V differs from that for Li-Si equilibrium compound formation (Fig. 4.3) in its absolute value of voltage and with its absence of voltage steps.

Figure 4.3 Composition dependence of equilibrium potential in the Li-Si system at 415°C.¹³
Figure 4.4  Calibrated XRD comparisons of a) reference XRD pattern of the starting mixture of Si:Ni:PVDF (60:30:10 weight ratio), b) Si sample lithiated to 69 mole% Li/ total Si, and c) Si sample lithiated to 57 mole% Li/ total Si, Notice no crystalline phase other than the Ni and the remaining Si phases is observed in c). In b), no expected Li-Si intermediate phases could be detected, only unidentified broad peaks at $\theta = 39.42^\circ$, $41.26^\circ$ and $43.08^\circ$. 
**Figure 4.6** Comparison of a vapor-deposited amorphous Si film (a), and the Si sample electrochemically lithiated to 68 mole% Li (b), showing similarities in the intensity profile as a function of scattering vector ($k$-vector).
Figure 4.5  HREM bright field images (a,c) and their corresponding dark field images (b,d) showing microstructure of Si after lithiation to 68 mole% Li. The sample mainly shows an amorphous phase which was predominantly composed of Si.
Figure 4.7  \( \text{Li}_{12}\text{Si}_7 \) unit cell (space group Pnma (No. 62)); \( a=8.61.0, b=19.734, c=14.241 \, \text{Å} \) is presented with Li atoms in large circles and Si in small circles. The compound forms orthorhombic crystals with \( \text{Si}_5 \) planar rings accompanied by star-shaped trigonal planar \( \text{Si}_4 \) clusters.\(^{19} \)
Figure 4.8 Four different possibilities as Li⁺ is driven to a metal anode: (I) Plating of Li metal on the surface, (II) Supersaturation of Li in the metal anode, (III) Alloying of Li with the metal (moving boundary), and (IV) Solid-state amorphization of Li-metal alloy.
Figure 4.9 Schematic Gibbs-free energy diagram of the Li-Si anode based on the data from Ref. 20 and 21 and the electrochemical data obtained on the amorphous Li-Si, showing the amorphous Li-Si phase as a metastable phase which forms if the formation of thermodynamically stable Li-Si crystalline phases (shown in ⊙) are kinetically suppressed.
Figure 4.10 Voltage profile of Si sample lithiated to a higher lithiation state (2166 mAh/g, 2.26 molar ratio of Li/total Si, 69 mole% Li) than the sample in Fig. 4.2. A similar voltage profile, with a plateau at ~0.1 V, is observed in this sample.
Figure 4.11  Li-Si phase diagram showing numerous intermediate phases. The trajectory shown corresponds to the composition of the electrochemically lithiated Si shown in Fig. 4.10.\textsuperscript{14}
Figure 4.12 HREM bright field image a) at low magnification, b) at high magnification, and c) a corresponding dark field image of (b), showing microstructure of Si after lithiation to 74 mole% Li. The sample mainly shows an amorphous phase, which was predominantly composed of Si.
Figure 4.13 HREM bright field images of a Si particle of a sample lithiated to 74 mole% Li at a) low magnification and b) at high magnification. The sample consists mainly of an amorphous phase, which was predominantly composed of Si. However, this image also shows nanocrystallites intimately mixed with the amorphous phase.
Figure 4.14 Schematic Gibbs-free energy diagram of the Li-Si anode based on the data from Ref. 20 and 21 and the electrochemical data obtained on the amorphous Li-Si. Note that in addition to the amorphous metastable phase, lithiation to 74 mole% Li also produces a metastable crystalline phase. This is consistent with the HREM and XRD observation of nanocrystallite in contrast to the Si lithiated to 68 mole % Li.
Figure 4.15 XRD data from the thin film solid-state reaction of Li with Si at a molar ratio of 2.816 Li/Si (74 mole% Li, as for Fig. 4.14). None of the expected equilibrium crystalline Li-Si compounds associated with this overall composition are observed. (by Dr. Y-I Jang, Oak Ridge National Laboratory, Oak Ridge, TN)
Figure 4.16  Voltage profiles of Sn samples lithiated to an average composition of a) 2.98 molar ratio of Li/Sn (75 mole% Li), and b) 0.4 molar ratio of Li/Sn (28 mole% Li). Note that, as in the case of Si, these samples also display a voltage profile that is not consistent with the formation of equilibrium crystalline phases (Fig 4.18).
Figure 4.17 Average composition of the Sn sample shown in Fig. 4.16a
Figure 4.18 Composition dependence of equilibrium potential in the Li-Sn system at 25°C and 400°C.\textsuperscript{22}
Figure 4.19 Calibrated XRD comparisons of a) reference XRD pattern of the starting mixture of Sn:Ni:PVDF (40:50:10 weight ratio), b) Sn sample lithiated to 28 mole% Li, and c) Sn sample lithiated to 75 mole% Li. Notice no crystalline phase other than the Ni and the remaining Sn phases is observed in b and c. In addition, no expected Li-Sn intermediate phases could be detected, only unidentified broad peaks at $2\theta = 38.58^\circ$, $55^\circ$ and $69.52^\circ$. 

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Figure 4.20 XRD data from the thin film solid-state reaction of Li with Sn at a molar ratio of 4.4 Li/Sn. None of the expected equilibrium crystalline Li-Sn compounds associated with this overall composition are observed. In addition, broad low intensity peaks at the same position as those found in the electrochemically lithiated Sn powder samples have been detected.

(by Dr. Y-I Jang, Oak Ridge National Laboratory, Oak Ridge, TN)
Figure 4.21  Voltage profile of Ag sample lithiated to an average composition of 1.11 molar ratio of Li/Ag (53 mole% Li). From the electrochemical data obtained, it was found that the sample exhibited a voltage plateau at ~ 1.25 and 1.5 V at an early stage of lithiation and a lower voltage plateau at 0.08 V. The higher plateaus were attributed to oxidation of the sample.
Figure 4.22  Ag-Li phase diagram showing numerous intermediate phases. The trajectory shown corresponds to the composition of the electrochemically lithiated Ag shown in Fig. 4.21.\textsuperscript{24}
Figure 4.23 Calibrated XRD comparisons of a) reference XRD pattern of the starting mixture of Ag:Cu:PVDF (40:50:10 weight ratio), b) Ag sample lithiated to 45 mole% Li. Results were consistent with some equilibrium crystalline phase formation. However, the amount of Ag present in the detected crystalline phases did not account for all of the Ag in the sample, suggesting some formation of an amorphous phase.
Figure 4.24 Voltage profile of Al sample lithiated to an average composition of 0.93 molar ratio of Li/Al (48 mole% Li) From the electrochemical data obtained, it was found that the sample exhibited a voltage plateau at 0.25 V which is slightly lower than 0.36 V, corresponding to the formation of equilibrium crystalline LiAl phase. This suggests formation of crystalline LiAl.
**Figure 4.25** Li-Al phase diagram showing numerous intermediate phases. The trajectory shown corresponds to the composition of the electrochemically lithiated Al shown in Fig. 4.24.²⁶
Figure 4.26  Calibrated XRD comparisons of a) reference XRD pattern of the starting mixture of Al:Cu:PVDF (70:20:10 weight ratio), b) Al sample lithiated to 48 mole% Li. Results were consistent with some equilibrium crystalline phase formation and little or no amorphous phase formation.
Figure 4.27 Structure of LiAl intermediate phase, having a BCC related, NaTl type structure.\textsuperscript{26}
Chapter 5

Conclusions

5.1 Summary

The primary objective of this thesis was an insight into the production of anode materials for Li-ion batteries which exhibit the high intrinsic gravimetric and volumetric capacities theorized for pure metal anodes, yet have good cyclability. To that end, an investigation with the following 2 approaches was undertaken. First, as Me-oxide materials have been presented in the literature as viable replacements for pure Me anodes due to their improved cyclability, an attempt was made to understand and thus correct, via processing techniques, the major drawback associated with these systems, which is a high first cycle irreversibility. Second, the issue of cyclability in metal anodes was itself addressed, via an investigation of a variety of systems, in order to improve the fundamental understanding of the failure mechanisms of these materials during electrochemical cycling. The combination of characterization techniques (XRD, SEM, HREM) on lithiated and delithiated anode materials, and engineering-level investigations (electrochemical testing of anodes in a battery setup) allowed, for the first time, a systematic and quantitative association of microstructural evolution with electrochemical behavior, for anode material candidates.
In this thesis, a thermochemical process based on the partial reduction of mixed oxides has been introduced as a new method for creating ultrafine metal-ceramic composites for Li-ion battery electrodes. Several mixed oxide systems have been identified as possible candidates for partially reduced metal-metal oxide composite anodes. Examples were given in Sb-V-O, Sb-Mn-O, Ag-V-O, Ag-Mn-O and Sn-Ti-O systems. It was demonstrated that the first-cycle irreversibility losses could be decreased relative to the unreduced metal oxides, due to the avoidance of Li$_2$O formation that otherwise occurs during displacement reactions of metal oxide anodes. Reversible charge capacities of 200-350 mAh/g (1100-2200 mAh/cm$^3$) were obtained. The effect of different material structures before partial reduction on differences in microstructure after reduction, as well as subsequent differences in electrochemical behavior, was discussed. It was shown that internal reduction products in which the reduced metal is captured inside the oxide matrix occurs in systems with fast oxygen diffusion (i.e. Sb$_2$Mn$_2$O$_7$ distorted fluorite) or low reduced metal concentration (i.e. Ag$_2$V$_4$O$_{11}$). These systems offer better cycle life than systems in which external reduction occurs. This is probably due to finer metal dispersion and passivation of the oxide matrix against side reactions such as chemical attack, which was later identified in this study as one of the possible causes of failure of metal anodes.

Before this study, failure of metal anodes was thought to have been solely caused by large volume changes during lithiation and delithiation leading to fracture of metal particles and loss of electrical contact. In this study, the morphology and internal structure of various particulate metal anodes was examined before and after lithiation, with XRD, SEM and HREM, in an attempt to understand the underlying causes of
fracture of metal anodes leading to capacity loss during electrochemical cycling. It was found that after one lithiation cycle, fracture was observed in particles of large size (>1μm), which was consistent with the fracture model proposed by Huggins and Nix. However, for all metals tested, the intact cycled metal was also found to form nanocrystallites (<15nm), some mixed with an amorphous phase. These nanocrystallites appeared to form due to high density nucleation of the lithiated phase. When observed after 50 cycles (at maximum capacity range), Sb displayed dispersed nanocrystalline particles of the same size as the nanocrystallites initially observed. This result suggested that a different failure mechanism of these materials systems acts over extended cycles, after which high volume changes no longer drive crack growth; chemical degradation was proposed as a possible failure mechanism. This result was in agreement with the high cyclability observed in internally reduced (and thus passivated) Me oxide anodes in Chapter 2.

Observations of highly disordered phase under HREM during the above investigation prompted a systematic investigation of such a phenomenon. A new mechanism, electrochemically-induced solid-state amorphization was proposed and explored. Experimental observations of various Me systems subjected to different degrees of lithiation supported such phenomenon. Using Li-Si as a model system, microstructural data from XRD and HREM were found to corroborate well with electrochemical data, providing strong evidence that suppression of the formation of equilibrium crystalline phases can occur in lithiated metals. A thermodynamic and kinetic rationale for such solid-state amorphization was presented along with supporting experimental data on a conventional solid-state bilayer thin film. Other bulk Li-Me
systems were also investigated and the corresponding results were also shown. These investigations, in conjunction with the content of Chapters 2 and 3, comprise the first systematic study of the evolution of microstructure in lithiated metal anodes, via direct and indirect quantitative observation, and the effects of that evolution on electrochemical behavior. As mentioned in the future work section of this chapter, such observations provide a strong direction for subsequent investigations, leading to continued improvement of Li-ion battery anode materials.

5.2 Future Work

Despite the many contributions of this work to the understanding of the structure-processing-property relation of anode materials for rechargeable Li-ion batteries. A number of opportunities for further investigation exist. First, in this work, a process, based on the concept of partial reduction was presented and tested, and resulted in anode materials that showed better cyclability than pure metal anodes and decreased 1st cycle irreversibility relative to previous metal oxides anode materials studied. However, the exploration of other ternary oxides, or nitride systems could lead to a further improvement of the properties described above. Regarding cyclability of and failure mechanism in pure metal anodes, future investigations could include a systematic variation of parameters known to be associated with chemical attack, i.e. electrolyte composition, temperature. Finally, in this thesis, the new phenomenon of electrochemically-induced solid-state amorphization was described. It would be interesting, therefore, to repeat the same systematic electrochemical tests and subsequent
characterization of a series of amorphous metals noting in particular their cyclability, in order to understand the value of using such materials for anodes.
Appendices

Appendix A. Possible Ternary Oxide Compounds for Partially Reduced

Anodes

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Appendix B. Quantification of Relative Amount of Crystalline Phases

Before and After Lithiation by Calibrated XRD

The procedure described here follows the method described in Chapter 14, p. 411-417 in Cullity, B. D. *Elements of X-Ray Diffraction*, Addison-Wesley, Reading MA. 1978. The examples shown here are specific to the method used in this thesis.

B.1 Direct Comparison Method

This method does not require a reference XRD sample with known amount of all the possible phases that could appear in the sample after lithiation, but a known relative amount of inactive phases and other starting phases. This method could be used to measure the amount of each crystalline phase (including the Li-Me alloys) in a lithiated sample. This is useful for quantifying the total amount of an element existing in various crystalline forms.

From the diffracted intensity equation of (Eq. 14.1, Cullity),

\[
I = \frac{I_0 A \lambda^3}{32\pi r} \left( \frac{\mu_0}{4\pi} \right) \frac{e^4}{m^2} \left( \frac{1}{v^2} \right) \left[ |F|^2 p \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] \left( \frac{e^{-2\mu}}{2\mu} \right) \tag{B.1}
\]

\( I \) = integrated intensity per unit length of diffraction line (J. sec\(^{-1}\). m\(^{-1}\)),

where \( I_0 \) = intensity of incident beam (J. sec\(^{-1}\). m\(^{-2}\))

\( A \) = cross-sectional area of incident beam (m\(^2\))

\( \lambda \) = wavelength of incident beam (m)

\( r \) = radius of diffractometer circle (m)

\( \mu_0 = 4\pi \times 10^{-7} \text{ mkg C}^{-2} \)

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\( e \) = charge on electron (C)
\( m \) = mass of electron (kg)
\( \nu \) = volume of unit cell (m\(^3\))
\( F \) = structure factor
\( p \) = multiplicity factor
\( \theta \) = Bragg angle
\( e^{2M} \) = temperature factor
\( \mu \) = linear absorption coefficient (m\(^{-1}\))

By putting

\[
K_2 = \left( \frac{I_0A^2}{32\pi r} \right) \left( \frac{\mu_0}{4\pi} \right)^2 \left( \frac{e^4}{m^2} \right) \left( \frac{1}{\nu^2} \right)
\]

(B.2)

and

\[
R = \left( \frac{1}{\nu^2} \right) \left| F \right|^2 \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \left( e^{2M} \right)
\]

(B.3)

the diffracted intensity is then given by

\[
I = \frac{K_2 R}{2\mu}
\]

(A.4)

where \( K_2 \) is a constant and \( R \) depends on \( \theta \), hkl, and the substance.

When the material is a mixture of different phases, the total intensity represents contributions of the different phases, which each vary linearly with the volume fraction of those phases, \( c_\alpha \). The linear absorption coefficient \( \mu \) also becomes \( \mu_m \), the linear absorption coefficient of the mixture. The intensity of phase \( \alpha \) and \( \gamma \) can then be written as:

\[
I_\alpha = \frac{K_2 R_\alpha c_\alpha}{2\mu_m}
\]

(B.5)
\[ I_y = \frac{K_y R_y c_y}{2 \mu_m} \]  \hspace{1cm} (B.6)

By dividing Eq. B.6 by Eq. B.5, we obtain
\[ \frac{I_y}{I_a} = \frac{R_y c_y}{R_a c_a} \]  \hspace{1cm} (B.7)

Since the total concentration of the mixture is
\[ c_y + c_a + ... = 1 \]  \hspace{1cm} (B.8)

We can use these equations to find the volume fraction of each phase knowing the value R (calculated from Eq. A.3) and by obtaining integrated intensity value, from the XRD pattern. The volume fraction obtained can be converted to a weight fraction and then a mole fraction by multiplying with the density of the phases and their molecular weight, respectively.

Relative amounts of each element existing in various crystalline forms with respective to the reference phase can then also be calculated by converting number of moles of a phase to number of moles of each element in the phase. Since the amount of the reference phase is constant and the relative amount of the starting phases relative to the reference phase is known, the amount of the other phases relative to this reference phase after lithiation can be obtained by comparing the concentration ratio of phases of interested and the reference phase before and after lithiation.

**B.2 Internal Standard Method**

This method requires integrated intensities of the same reference peak in the sample before and after lithiation and cannot be used to obtain information of a phase that does
not exist in the starting mixture. Equation B.7 can be written for $\alpha$ and $\gamma$ phase before and after lithiation as

\[
\frac{I_{r, before}}{I_{a, before}} = \frac{R_{\gamma}c_{\gamma, before}}{R_{\alpha}c_{\alpha, before}}
\]  \hspace{1cm} (B.9)

and

\[
\frac{I_{r, after}}{I_{a, after}} = \frac{R_{\gamma}c_{\gamma, after}}{R_{\alpha}c_{\alpha, after}}
\]  \hspace{1cm} (B.10)

respectively. By dividing Eq. B.9 by B.10, we get

\[
\frac{I_{r, before}}{I_{a, before}} \cdot \frac{I_{a, after}}{I_{r, after}} = \frac{c_{\gamma, before}}{c_{\gamma, after}} \cdot \frac{c_{\alpha, after}}{c_{\alpha, before}}
\]  \hspace{1cm} (B.11)

Let $\gamma$ be the reference phase. Then $c_{\gamma, before} = c_{\gamma, after}$ yielding

\[
\frac{c_{\alpha, after}}{c_{\alpha, before}} = \frac{I_{r, before}}{I_{r, after}} \cdot \frac{I_{a, after}}{I_{a, before}}
\]  \hspace{1cm} (B.12)

from which the relative concentration of $\alpha$ phase before and after lithiation can be calculated.
Appendix C. XRD Scans of Lithiated Ag Immediately After Lithiation and After 13 Days of Storage in an Ar-fill Glovebox

Ag sample lithiated to 45 mole % Li (Fig. 4.21) a) the same sample after 13 days of storage in Ar at room temperature and b) X-rayed scan of the sample immediately after lithiation.