Metallic Coatings on Intermetallic Anodes:
A Study in Low Temperature Deposition

An Honors Thesis (HONRS 499)

By

Jessica Clevenger

Argonne National Laboratory
Argonne, IL 60439
Research Supervisor: Dr. John T. Vaughey

Ball State University
Muncie, IN 47306
Thesis Advisor: Dr. James P. Rybarczyk

April 1, 2005

Expected Date of Graduation: May 7, 2005
Note: In addition to fulfilling the requirements of the Honors Thesis (HONRS 499) at Ball State University, this thesis was prepared in partial fulfillment of the requirements of the Office of Science, Department of Energy's Student Undergraduate Laboratory Internship (SULI) Program under the direction of research supervisor Dr. John T. Vaughey in the Chemical Engineering Division at Argonne National Laboratory during the summer of 2004.
Argonne National Laboratory, a U.S. Department of Energy Office of Science laboratory, is operated by The University of Chicago under contract W-31-109-Eng-38.

---

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor The University of Chicago, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or The University of Chicago.
# TABLE OF CONTENTS

DISCLAIMER ............................................................................................................................... iii

ABSTRACT ..................................................................................................................................... 2

INTRODUCTION .......................................................................................................................... 3

MATERIALS AND METHODS .................................................................................................... 7

RESULTS AND DISCUSSION ................................................................................................... 11

CONCLUSION ............................................................................................................................. 19

ACKNOWLEDGMENTS ............................................................................................................ 20

REFERENCES .......................................................................................................................... 21

TABLES ...................................................................................................................................... 22

FIGURES .................................................................................................................................... 24
ABSTRACT

Lithium-ion batteries have rapidly become important components of many devices that require portable power, be it a CD player, implanted medical device, or hybrid-electric automobile. The battery has three main parts – a cathode where reduction occurs (usually a highly oxidized metal oxide), an organic electrolyte to conduct ions, and an anode where oxidation occurs (usually lithium metal or graphite). In many of these devices, the anode is the limiting factor in either device performance or device cost. Present anodes work well, but have many safety issues – notably overcharge problems or lifetime problems related to lithium’s unique electrochemistry. Alternative anode materials, typically Sn- or Sb-based alloys, have several problems, including high irreversible capacity, which is the amount of lithium inserted on the first charge that does not return to the anode on discharge. A significant amount of this “lost lithium” is involved in side reactions on the anode surface between the charged anode, e.g. Li$_3$Sb, and the organic electrolyte forming insoluble lithium salts and complexes. The purpose of this study was to attempt to lower the irreversible capacity by adding silver to the electrode surface, thereby altering the interface between the electrode and the electrolyte.

Silver coatings were deposited on anodes using four different methods: (1) silver salt reduction by aldehydes, (2) in-situ decomposition of silver salts in the electrolyte, (3) a surface coating of an insoluble silver salt, and (4) a physical mixture of silver metal and the active material. Each method was found to produce different results. The silver coatings via the aldehyde reduction (Tollens Reaction) improved the performance of the cells containing synthetic (GDR) graphite, while cells using a Cu$_6$Sn$_3$ alloy were less pronounced, although it seemed to increase rate capability. The in-situ deposition method decreased the irreversible capacity for the Cu$_6$Sn$_3$ anode, while the ball-milled physical mixture made the irreversible capacity worse, probably due to the oxidation of the underlying electrode materials. Overall, silver coatings look very promising, but more work needs to be done yet.
INTRODUCTION

Batteries are used in a variety of commercial products, ranging from cell phones, to children’s toys, to medical devices. They all have in common the need to power a mobile device for a substantial period of time. In commercial batteries, the anode (negative electrode) is typically either graphite or lithium metal. However, since they both work at the same very low potential and display high reactivity with the electrolyte, alternatives are being sought for safety reasons [1]. Additionally, in many of these devices, the anode is also the limiting factor in either device performance or cost. It has been estimated by Fuji that up to 1/3 the cost of a commercial lithium-ion battery originates from the anode and its related safety circuits [2]. One important need is to replace lithium metal in medical devices, such as implantable cardiac defibrillators, medical devices used in patients known to have cardiac fibrillation or tachycardia. When the heart’s electrical activity becomes disordered, the ventricles can flutter – cardiac fibrillation – or cause an extremely rapid heartbeat – cardiac tachycardia. In either case, the device senses the arrhythmia, delivers one or multiple shocks to the heart, returning the heart to a normal rhythm [3]. These devices currently use lithium-ion batteries because they offer the high voltage and power necessary to restart the heart before oxygen deprivation sets in, resulting in other medical problems, e.g. stroke. Because they need to have a long lifetime in the body before use, there is much effort to maintain the reactivity of the lithium metal anode. The problem is that over such a long time (7-10 years), the anode can develop a passivation coating from gradual and continuous reaction with the electrolyte that slows down its kinetics. Replacing the lithium may offer a way to increase the cell’s required stability towards the organic electrolyte. Other possible uses include safer and longer lived batteries for hybrid electric cars and consumer electronics.

Since lithium is the lightest of all metals, has the greatest electrochemical potential, and provides the largest energy density for weight, it can meet today’s demands placed on the energy
storage capabilities of batteries. However, because of lithium metal’s inherent instability (high reactivity with air and the production of H\textsubscript{2} gas), research has shifted towards using lithium ions instead. Although slightly lower in energy density than lithium metal-based batteries, the lithium-ion battery concept is considered safer, provided certain precautions are met when charging and discharging. Lithium ion batteries offer a high cell voltage of 3.6-4.3 volts, allowing battery pack designs with only one cell, saving on safety electronics, minimizing internal connections, and simplifying cell construction [4].

A battery consists of three basic parts -- two electrodes (a cathode and an anode) separated by a physical separator (typically a porous polyethylene sheet), and an electrolyte to conduct ions. Lithium-ion batteries use lithium host substrate materials for the electrodes (such as LiCoO\textsubscript{2} for the cathode and graphite for the anode), and the lithium ions are shuttled between the cathode and anode during charge and discharge. Electrochemical reactions at the electrodes produce an electric current that powers an external circuit [5].

Since the beginning of battery manufacturing in the 1860's, carbon materials have always proven to be very useful as components of the electrodes because of their high electrical conductivity and electrochemical stability. However, all carbon materials experience irreversible
side reactions during the first electrochemical insertion of lithium ions. In a lithium-based system, these reactions consume the active lithium by irreversibly producing surface compounds, e.g. Li₂CO₃, LiOH, and LiOR (R = alkyl groups), that have to be minimized since they lead to a capacity loss – the irreversible capacity [7]. These compounds, formed because the electrolyte is unstable at low potentials, are insoluble, electronically insulating products that coat the surface of the electrode. This passivating layer on the carbon or any other anode material is called the solid electrolyte interphase (SEI) [8]. There have been recent reports that certain alloy anodes have SEI layers that are rich in polymerized organic electrolytes rather than their lithium salts, and this may be a novel way to reduce irreversible capacity since lithium won’t be consumed by this side reaction [2,8].

In this project, we altered the interface between the electrolyte and electrode by using surface coatings to minimize the loss of lithium in the formation of these insulating species and to minimize the thickness of the SEI layer. This interface is one of the leading causes of slow electrochemical reactions in the battery: a charge transfer reaction. Speeding up the charge transfer will allow for quicker charge recovery, with consequent more rapid power response available, for example, for repeated shocks to the heart in an implantable cardiac defibrillator or a faster electronic response from automobile brakes. Previous work has shown that such coatings can be a viable solution to this problem by “engineering” the interface. Arnold et al. [9] have reported that improvements in the rate capability of the cathode material LiFePO₄ can be achieved by using small particles with an electronic and ionic conductive particle coating. Cho [10] has suggested that an AlPO₄-nanoparticle coating on the LiCoO₂ surface improves the thermal stability and electrochemical performance of LiCoO₂ cathodes at high voltages by reducing the activity of the oxide anions at the surface. Vollmer et al. [11] have shown that in-situ coatings of anodes using organic monomers, e.g. vinyl ethylene carbonate, which polymerize
to form ion-conducting polymers, can also be a promising alternative by coating the active surface before the electrolyte reacts.

The goal of this project was to decrease the irreversible capacity of common anodes by coating the surface of the electrode materials with silver to reduce the reactions with the electrolyte, and to assess several methods of coating to determine differences in coating or morphology. Yoshida et al. [12] have investigated the use of multiple metals as coatings, one of which is silver. Their work on carbon fibers has shown that silver-coated materials have less reactivity with common electrolyte solvents in comparison to copper-coated materials. Son et al. [13] have studied the effects of silver coatings on LiMn$_2$O$_4$, a cathode material. They found that the LiMn$_2$O$_4$ treated with a silver coating gives higher charge-discharge capacity and lower cell polarization than an untreated electrode. Thus, this evidence suggests that the addition of silver coatings might be the improvement needed.
MATERIALS AND METHODS

Part I

Silver Coatings: An Application of the Tollens Test for Aldehydes

The Tollens reaction, important in organic chemistry, is routinely used as a qualitative test for the presence of aldehydes. During the reaction, Ag$^+$ is reduced to Ag metal, while an aldehyde is oxidized to a carboxylic acid. The silver metal is deposited atomically on a surface, such as the glass surface of a flask, creating a silver mirror. By mixing the active electrode material into the solution before addition of the aldehyde, the majority of the silver “mirror” can be deposited onto the electrode substrate.

Solid AgNO$_3$ (Aldrich, 99+%) was dissolved in 70°C distilled water, and the electrode material to be coated was also placed in the beaker. While vigorously stirring with a magnetic stir bar, excess formaldehyde (Aldrich, 37 %wt in water) was added; this resulted in immediate coating of silver metal onto the electrode material. Appropriate amounts of AgNO$_3$ were used to yield 1%, 3%, 5%, 10%, and 15% by weight silver coatings on the electrode material. These silver coatings were deposited on two commercially available carbons – a natural graphitic material (Chinese) and a synthetic graphite (GDR-AA-4, Switzerland) – and on another electrode material, Cu$_6$Sn$_5$ (ANL, 98%). After filtering, the coated electrode powders were dried in air at 75°C overnight. See Figure 1 for the structure of Cu$_6$Sn$_5$ and Figure 2 for the lithiated Cu$_6$Sn$_5$: Li$_2$CuSn. In Figure 2, the red atoms represent the lithium inserted into the [CuSn] framework. Scanning electron microscopy (SEM) photos were taken to document the resulting coatings of Ag. The materials were also investigated by powder X-ray diffraction.

Part II

Silver Coatings: In-Situ Deposition

In-situ deposition of silver was performed by first preparing two silver electrolyte solutions, one prepared from reagent AgNO$_3$ salt and the other from AgClO$_4$ salt. Each silver
salt was dissolved into the electrolyte, which was then used in cell construction. A 0.5 % wt AgNO₃ dissolved in LP40 (50 % wt EC (ethylene carbonate) / 50 % wt DEC (diethyl carbonate), 1 M LiPF₆, Merck KG) solution was prepared in an argon-filled glove box and placed into a 75°C oven overnight. In addition, a 4.6 % wt AgClO₄ dissolved in Gen 3 electrolyte (40% DEC / 30% PC (propylene carbonate) / 30% EC with 1.0 M LiPF₆, ANL) was prepared and tested.

Part III

Silver Coatings: Silver Salt Surface Coating

Multiple silver salts were made by dissolving solid AgNO₃ in distilled water, adding various organic acids, and filtering the new insoluble silver salt. The following organic acids were used to prepare their corresponding silver salts: succinic acid disodium salt (Aldrich, p.a. 99%), fumaric acid disodium salt (Aldrich), L-ascorbic acid (Aldrich, p.a. 99+%), and oxalic acid dihydrate (Aldrich, 97%). The materials were examined by powder X-Ray diffraction and evaluated electrochemically for their reduction potentials.

Part IV

Silver Coatings: Physical Mixture

Two separate silver-coated anode materials were made as physical mixtures. One sample was made as a 2 % wt Ag metal (Mallinckrodt, precipitated powder) mixed by hand with Cu₆Sn₅ and shaken in a Nalgene bottle. The second sample was made by high energy ball-milling 2 % wt Ag metal (Mallinckrodt, precipitated powder) mixed by hand with Cu₆Sn₅, with 5 % wt graphite as a solid lubricant.

Part V

Lamination and Electrochemical Techniques

All active electrode powders (Chinese graphite, synthetic GDR graphite, and Cu₆Sn₅ – with and without silver coatings) were thoroughly mixed using a mortal and pestle into a slurry using the following amounts of materials: 80 % wt active electrode powder, 10 % wt acetylene
black (Chevron, C-55), and 10%wt 13% PVdF/NMP (polyvinylidene difluoride in N-methyl pyrrolidone). Acetylene black is an additive commonly used in electrodes to enhance electronic conductivity, and since it does not react with lithium, it does not affect the observed capacity. PVdF, similar to Teflon, acts as an adhesive to hold the electrode mixture together and to attach the electrode mixture to the current collector, copper. The slurry was spread evenly across a piece of copper foil taped to a glass sheet. It was then placed in an oven and dried by air at 75°C overnight to evaporate the NMP and to polymerize the PVdF, which binds the electrode materials to the copper foil. This process of binding a thin layer of electrode mixture to a thin layer of copper foil is called lamination. The laminate was then removed from the glass sheet and was fed through a press to even out the electrode thickness, reduce porosity, and to increase conductivity. Electrodes were punched out from the laminate using a hammer and electrode punch of appropriate size. See Figure 3.

Before building the cells, the active electrode mass was determined by weighing the punch (electrode materials + copper foil), subtracting the mass of a copper punch of equal diameter, and multiplying by 0.80 (since the active material is 80% of the total electrode mixture weight). This active weight calculation was later used in capacity (mAh/g) calculations. Electrochemical cells were then constructed in an argon-filled glove box or in a dry room, with lithium metal as the negative electrode. The electrodes were separated by a Celgard polypropylene separator, which is permeable to Li ions but not electrons. The electrolytes used were LP40, Gen 2 (70% DEC / 30% EC 1.2 M LiPF₆), or the previously mentioned electrolytes prepared for in-situ deposition. Cells were tested on a Maccor (Tulsa, OK) battery cycling station, discharging and charging in a specified voltage window under constant current. Of particular interest was the determination of the capacity for each cycle (a cycle is one discharge and charge) and the change in capacity over a number of full cycles. The irreversibility capacity could be easily calculated by finding the difference in capacity from cycle 1 to cycle 2. The
amount of lithium passed between the electrodes, as well as voltage profiles, was monitored by the Maccor cycling software, measuring all electrochemical data during charging and discharging. Cells without silver coatings were built and tested for comparison purposes. See Tables 1-4 for electrode materials, electrolyte used, and charge/discharge potential.
RESULTS AND DISCUSSION

Table 5 lists the tested electrode materials and their discharge capacities. The theoretical capacities were determined by dividing the Faraday constant \((96500 \text{ C} = 26805 \text{ mAh})\) by the atomic weight of the delithiated active material, then multiplying by the number of lithiums that were expected to be stored. The irreversible capacity was calculated as \([(\text{cycle 1} - \text{cycle 2})/\text{cycle 1}] \times 100\%\).

Part I

Silver Coatings: An Application of the Tollens Test for Aldehyde

Silver coatings were prepared by this method on Chinese graphite, GDR graphite, and Cu₅Sn₅. The early part of this project focused on Chinese graphite, but problems arose with cycling, probably caused by the binder interacting with the rough surface edges of the graphite and the reactivity of the silver. See Figure 4 for a time profile of the Chinese graphite. In this figure, it took approximately one hour for the first discharge (i.e., it took one hour for all of the Li ions the carbon could take up within this voltage window to migrate across the separator from the lithium metal anode). However, these Li ions were not then subsequently released upon charging, because the charging lasted for less than a second – this is the peak observed at one hour. This continued for the next several cycles until the cell completely failed (around 4.5 hours where it began to cycle multiple times per second). This failure eliminated the Chinese graphite from further consideration and experimentation.

At this point, the round-edged synthetic GDR graphite was focused on, resulting in much better cycle-ability as seen in Figure 5. In this figure, the first discharge to nearly 0 volts lasted until approximately 30h, the following charge required a further 20h, and so on. This cycling pattern remains consistent throughout the time profile; thus, it had much better cycle-ability than the Chinese graphite from Figure 4. Figures 6, 7, and 8 show similar time profiles for GDR graphite with 1%, 3%, and 5% silver coatings respectively. Not much difference can be seen
among these profiles, other than the different amounts of time required to complete a total charge/discharge cycle. However, this time period apparently had nothing to do with the materials, but rather with what the current (mA) setting was. If the current was set too high or too low, the cell would cycle too fast or extremely slow. All of the cells in these figures cycled slowly; optimally, cells should cycle about 5 times per 24-hour day.

More important, however, were the capacity calculations. Again, the goal was to minimize the amount of capacity loss caused by the electrode surface. The discharge capacities are compared in Figure 9, and the relative % irreversible capacities are compared in Figure 10. In Figure 9, the graphite with no Ag coating had the largest drop in capacity from cycle 1 to cycle 2. Thus, it had the highest irreversible capacity (% capacity loss from cycle 1 to 2) as shown in Figure 10. The graphite with silver coatings had smaller decreases in capacity from cycle 1 to cycle 2; therefore, the silver coatings decreased the irreversible capacity. A low irreversible capacity is desirable. The 1% Ag coating appeared to produce the best results. Although the coating was used to protect the electrode surface, silver also has some reactivity with lithium, forming Li$_x$Ag alloys around 100-200 mV (vs. Li). In low amounts, the silver probably settled on the most reactive spots on the graphite surface, impeding reactions with the electrolyte. However, as extra silver was added, it probably randomly coated the surface, and as it alloyed with lithium, it slightly increased the irreversible capacity. Lithium-silver alloys are known to have very slow kinetics and only under slow charge conditions is the alloying reaction reversed. These studies indicate that 1% wt is the optimal amount of silver.

Figures 11-14 show the time profiles for Cu$_6$Sn$_5$ electrodes, with and without silver coatings. The discharge capacities are compared in Figure 15, and the irreversible capacities are compared in Figure 16. The cells were cycled in two different voltage windows, 2-0 V and 2-0.2 V. For the 2-0 V window, the lithium was inserted into the alloy completely and eventually extruded the copper, forming Li$_{4.4}$Sn and copper metal. Additionally, silver reacted with lithium
below 200 mV (vs Li), so in this voltage window it also lithiated. In the 2-0.2 V window, the amount of lithium inserted was less, but it fell short of addition to the silver metal and only filled up the alloy’s interstitial holes and did not extrude the copper. In Figure 11, the Cu$_6$Sn$_5$ cycled satisfactorily from 2-0 V for the first few cycles, but then apparently shorted, resulting in cell failure (the solid area in the time profile where the cell cycled multiple times a second).

Shorting or other rapid cell failures are usually caused by three mechanisms. First, there could be separator holes. The separator is what physically keeps the two electrodes separate. If there were holes in the separator (caused by either a faulty material from the supplier or unintentionally introduced during cell construction), the two metallic electrodes could touch each other and the cell would short. Second, de-lamination could occur, meaning the electrode loses its attachment to the copper current collector. Third, there could be lithium metal oxidation by the infiltration of air due to hardware (gasket) failure. During cell construction, the gasket seals the casing airtight, preventing outside air from entering the cell. In this study, the second mechanism discussed above was the most likely candidate for the cause of the failure, as the cells taken apart and examined did show some de-lamination. Additionally, comparing the volume change between Cu$_6$Sn$_5$ and silver metal and their lithiated products Li$_{4.4}$Sn and Li$_{3.3}$Ag indicated volume expansion of several hundred percent, which would overwhelm the binder. Typical binders are only capable of absorbing a 15-25% expansion. Much better cycling was observed using the 2-0.2 V window. With much less lithium inserted, the expected volume expansion was only 40% for the reaction of Cu$_6$Sn$_5$ with lithium to make Li$_2$CuSn. Although this was still outside the reported range, it was very close, since additional volume expansion was taken up by voids and pores in the electrode.

For the 15% Ag/Cu$_6$Sn$_5$, it was interesting to note that the silver thickness was probably too much for this sample, as the initial capacity was quite low but over a few cycles grew to the expected number of 250 mAh/g (Fig. 15). This may have occurred because the silver was
blocking a significant amount of the active alloy surface, and as cycling occurred, the silver diffused to grain boundaries or became incorporated into the SEI layer.

Overall, this method of silver coating worked very well. The procedure was relatively simple, but more time consuming than the other methods. The silver coatings also had a profound effect on electrochemical performance of the synthetic graphite (GDR) electrodes. As seen in Figure 10, there was a significant decrease in capacity loss, which was highly desirable. The silver coatings improved the irreversible capacity by an average of 39.65% compared to the electrode with no Ag added. The discharge capacity curves in Figure 9 also showed that the silver coatings had a positive effect.

However, for the Cu₆Sn₅ electrodes, as seen in Figure 16, the 5% and 15% coatings overall had little impact on cycling capacity. The 5% Ag coating had slightly higher irreversible capacity than the sample with no Ag. The 15% Ag actually gained capacity between cycles 1 and 2. Figure 15 also shows small difference in discharge capacity curves between the 15% Ag and the others. The 15% Ag electrode began with a capacity of 140 mAh/g and increased to about 235 mAh/g where it stayed fairly constant. The others, however, started off with a much higher initial capacity and then maintained it.

Presently, studies are planned to evaluate the silver coated materials for their rate capability (how quickly they can cycle before failure), together with an evaluation of the silver electrolyte interface using AC impedance spectroscopy as a function of cycle life.

Part II

Silver Coatings: In-Situ Deposition

During electrochemical testing, the silver ions in the electrolyte solution reduced to silver metal, followed by deposition onto the electrode surface at a particular voltage; thus, the silver coating was deposited in-situ. See Figure 17 for the time profile for Cu₆Sn₅ with 0.5% AgNO₃ in LP40 and Figure 18 for the time profile for Cu₆Sn₅ with 4.6% AgClO₄ in Gen 3. Both of these
figures show good cycle-ability, with consistent discharge and charge curves. Again, the capacity calculation was more important. Figure 19 compares the discharge capacities of these in-situ depositions to the discharge capacity of Cu₆Sn₅ with no Ag. It is clear from this figure that there was a much greater drop in discharge capacity from cycle 1 to 2 for the Cu₆Sn₅ with no silver coating, and a smaller capacity drop for the cells with in-situ deposition. Figure 20 compares these irreversible capacities, showing that the in-situ deposition had a profound effect on minimizing the irreversible capacity.

For these samples, the solution introduction of the silver was found to present problems that the Tollens method did not. During cell preparation, it was noted that the solution was stable. However, upon cell construction, the lithium metal in the cell turned black upon addition of the electrolyte. It is speculated that the lithium reduced the dissolved silver, which coated on the lithium; thus the black color. This would present problems later on during cell operation since the lithium now has a secondary layer through which to diffuse. This immediate reduction to metal of the silver cations coated the wrong electrode – the lithium metal. Experiments to coat the electrode with a silver salt and then decompose it in-situ to silver metal are currently underway but have not been finished (See "Silver Coatings: Silver Salt Surface Coatings").

When preparing the electrolyte solutions, it was noted that the silver nitrate salt appeared to be far less soluble in the electrolyte than the silver perchlorate, and this may be a reason for the slight differences in performance (Fig 20). As can be seen in this figure, there was a significant decrease in capacity loss. The in-situ deposition improved the irreversible capacity dramatically, by an average of 84.33% when compared to Cu₆Sn₅ with no Ag.

Part III

Silver Coatings: Silver Salt Surface Coating

These silver salts were only tested electrochemically to determine their reduction potential. In the future, silver salts will be coated on the anode and once the silver salt’s
reduction potential is reached during the first discharge, the silver will reduce to silver metal. This is an alternate way to yield a silver metal coating on the anode. Although still being studied, these experiments were meant to provide an alternative method to in-situ add silver to the surface. Since the solution-based samples produced early uncontrolled reduction on the wrong electrode, attempts to make several salts that could be precipitated on the correct surface and be reduced on the first discharge are planned. This is in contrast to the Tollens method where the silver was reduced before cell construction. In these experiments, several insoluble silver salts were synthesized and decomposed in-situ to determine their characteristics and decomposition voltage. Most were found to decompose near 2.0V (vs. Li). See Figure 21 for the time profile for silver oxalate. See Table 6 for a listing of the silver salts and their respective reduction potentials. Further work is in progress to utilize them as coatings.

Part IV

Silver Coatings: Physical Mixture

See Figure 22 for the time profile of 2 %wt Ag/Cu₆Sn₅. Discharge capacity curves can be seen in Figure 23, with their irreversible capacities shown in Figure 24. These studies were done as a control. Because the materials were synthesized as physical mixtures, the silver was not distributed evenly or of a small size. In these systems, the silver/alloy mixture would be expected to react as two separate components, a composite, and thus yield information on the activity of Ag in these systems. These controls showed that the cell failure observed above (Cu₆Sn₅, Tollens) when going to lower voltage was related to the material and maybe the silver, but not the process used to make the coating. For instance, cells are very sensitive to water, so if water were carried along from the deposition, the cell would fail. It failed here with no water involved in the process, thus it was a Cu₆Sn₅ and Ag phenomenon. Previous work had shown that although silver is active, it has very bad kinetics when reacting with lithium and may or may not alloy under the conditions used in this study. With limited cycling data, it appeared that the
silver addition in this way had a limited effect and reinforced the positive results from the \textit{in-situ} and Tollens surface coatings. This method was only used to construct a 2 \%wt Ag/Cu\textsubscript{6}Sn\textsubscript{5} electrode. The silver coating did not reduce the capacity loss in this case, and actually tripled it.

\textbf{Part V}

\textit{X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)}

Powder X-Ray diffraction (XRD) and scanning electron microscopy (SEM) were used to verify composition and to determine the consistency of the silver coatings. In XRD, the diffraction pattern was an indication of phase purity and composition. It was done primarily to see if the silver deposited, or if the ball-milling of Ag and Cu\textsubscript{6}Sn\textsubscript{5} alloyed the sample (to make AgSn) or just mixed them well. See Figure 25 for an XRD pattern for 1\% Ag/C-GDR and Figure 26 for an XRD for 1\% Ag/Cu\textsubscript{6}Sn\textsubscript{5}. The x-axis of \(2\Theta\) is the angle of diffraction (which comes from the distance between atoms in the structure) and the y-axis is intensity (which is proportional to the atomic number of the atoms). The peaks shown in both of these figures correspond to C or Cu\textsubscript{6}Sn\textsubscript{5}, respectively. The Ag peak could not be seen at such a low silver content in these samples. In addition, in the early stages of this project, the Tollens-type deposition was performed at 50\(^\circ\)C, but the XRD analysis showed no Ag metal deposited on either the Chinese or GDR graphite at this temperature even at silver concentrations where Ag should be easily seen by XRD. After obtaining these results, the Tollens reaction temperature was increased to 70\(^\circ\)C for all subsequent coatings, resulting in satisfactory coating.

In addition, XRD revealed that all silver salts prepared had the proper composition except for silver ascorbate, which was actually shown to be silver metal. See Figure 27 for the XRD for silver succinate, which shows that a single phase material, or pure sample, was made.

SEM was performed to determine the form the silver deposited as and its distribution. The Tollens type gave smaller particles than the physically mixed, and the ball-milled destroyed the morphology of the underlying Cu\textsubscript{6}Sn\textsubscript{5} particle. See Figure 28 for 5\% Ag/Cu\textsubscript{6}Sn\textsubscript{5} (ball-
milled) at 5,000X magnification. The white areas/grains are Ag. In contrast, see Figure 29 for 3% Ag/Cu₆Sn₅ at 2,300X magnification, Figure 30 for 3% Ag/Cu₆Sn₅ at 1,200X magnification, and Figure 31 for 1% Ag/Cu₆Sn₅ at 2,500X magnification – all coated by the Tollens method. From these photos, it appears that the silver precipitated on the surface coated as nanoparticles of approximate size 50-100 nm as opposed to seeing silver particles next to Cu₆Sn₅ particles. Annealing of these samples would probably even out the coating even further, as is done with chemical vapor deposition (CVD), but that was not evaluated due to concerns it may “dope” into the electrode material.
CONCLUSION

We have developed and evaluated three methods of coating copper tin alloys with silver for use as a lithium-ion battery anode. Previous work had shown that silver coated electrodes have better conductivity and lower irreversible capacity than uncoated electrodes, and we extended this work to other anode materials. In our study, ex-situ deposition of silver by the Tollens method was shown to make a nicely dispersed silver coating, while not affecting the observed anodes’ capacity. For a commercial graphite anode, a 1% Ag coating was found to be the optimum amount to decrease irreversible capacity by a strong 77%. For Cu₆Sn₅ electrodes, amounts of silver up to 5% were found to stabilize cycling and decrease initial capacity loss by 9%, almost by half. Alternative methods of in-situ deposition and physical mixing were found to be less effective, probably due to having less control over where the silver ended up in the cell.
ACKNOWLEDGMENTS

I want profusely to thank the U.S. Department of Energy and Argonne National Laboratory's Chemical Engineering Division for creating, organizing, and funding the Student Undergraduate Laboratory Internship program. Special thanks goes to my research supervisor Dr. John Vaughey for his knowledge, guidance, and humor. I also want to thank Dr. Vaughey for giving me such a fun and enjoyable research experience over the summer of 2004 and for his extra effort in helping me develop this thesis. In addition, I acknowledge Dr. Christopher Johnson and Dr. Art Kahaian for all their help in the labs.
REFERENCES


[6] Figure obtained from http://endomoribu.shinshu-u.ac.jp/research/1i-ion.


TABLES

Table 1: Constant Current Charging and Discharging for Chinese Graphite

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Ag/C-Chinese</td>
<td>LP40</td>
<td>1.5 to 0.01</td>
</tr>
<tr>
<td>10% Ag/C-Chinese</td>
<td>LP40</td>
<td>1.5 to 0.01</td>
</tr>
</tbody>
</table>

Table 2: Constant Current Charging and Discharging for GDR Graphite

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-GDR</td>
<td>LP40</td>
<td>1.5 to 0.01</td>
</tr>
<tr>
<td>1% Ag/C-GDR</td>
<td>Gen 2</td>
<td>1.5 to 0.01</td>
</tr>
<tr>
<td>3% Ag/C-GDR</td>
<td>Gen 2</td>
<td>2.0 to 0.01,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5 to 0.01</td>
</tr>
<tr>
<td>5% Ag/C-GDR</td>
<td>Gen 2</td>
<td>2.0 to 0.01</td>
</tr>
<tr>
<td>5% Ag/C-GDR</td>
<td>LP40</td>
<td>1.5 to 0.01</td>
</tr>
<tr>
<td>10% Ag/C-GDR</td>
<td>LP40</td>
<td>1.5 to 0.01</td>
</tr>
</tbody>
</table>

Table 3: Constant Current Charging and Discharging for Cu₆Sn₅

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₆Sn₅</td>
<td>LP40</td>
<td>2.0 to 0.2</td>
</tr>
<tr>
<td>Cu₆Sn₅</td>
<td>LP40</td>
<td>2.0 to 0.01</td>
</tr>
<tr>
<td>Cu₆Sn₅</td>
<td>0.5%AgNO₃ in LP40</td>
<td>2.0 to 0.01</td>
</tr>
<tr>
<td>Cu₆Sn₅</td>
<td>4.6%AgNO₃ in Gen3</td>
<td>2.0 to 0.0</td>
</tr>
<tr>
<td>2wt%Ag/Cu₆Sn₅</td>
<td>LP40</td>
<td>1.5 to 0.01</td>
</tr>
<tr>
<td>5% Ag/Cu₆Sn₅</td>
<td>LP40</td>
<td>2.0 to 0.01,</td>
</tr>
<tr>
<td>15% Ag/Cu₆Sn₅</td>
<td>LP40</td>
<td>2.0 to 0.2</td>
</tr>
</tbody>
</table>

Table 4: Constant Current Discharging for Silver Salts

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver succinate</td>
<td>LP40</td>
<td>discharge to 1.0</td>
</tr>
<tr>
<td>Silver fumarate</td>
<td>LP40</td>
<td>discharge to 1.0</td>
</tr>
<tr>
<td>Silver ascorbate</td>
<td>LP40</td>
<td>discharge to 1.0</td>
</tr>
<tr>
<td>Silver oxalate</td>
<td>LP40</td>
<td>discharge to 1.0</td>
</tr>
</tbody>
</table>
### Table 5: Discharge Capacities

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Theoretical Capacity (mAh/g)</th>
<th>Experimental Capacity (Cycle 1)</th>
<th>Experimental Capacity (Cycle 2)</th>
<th>Irreversible Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-GDR</td>
<td>371.95</td>
<td>320.50</td>
<td>265.49</td>
<td>17.16%</td>
</tr>
<tr>
<td>1% Ag/C-GDR</td>
<td>371.95</td>
<td>287.36</td>
<td>275.02</td>
<td>4.29%</td>
</tr>
<tr>
<td>3% Ag/C-GDR</td>
<td>371.95</td>
<td>350.72</td>
<td>303.26</td>
<td>13.53%</td>
</tr>
<tr>
<td>5% Ag/C-GDR</td>
<td>371.95</td>
<td>378.70</td>
<td>328.51</td>
<td>13.25%</td>
</tr>
<tr>
<td>Cu6Sn5</td>
<td>340/622</td>
<td>290.61</td>
<td>231.01</td>
<td>20.6%</td>
</tr>
<tr>
<td>Cu6Sn5 with 0.5%AgNO3 in LP40</td>
<td>340/622</td>
<td>546.75</td>
<td>510.22</td>
<td>6.68%</td>
</tr>
<tr>
<td>Cu6Sn5 with 4.6%AgClO4 in Gen3</td>
<td>340/622</td>
<td>621.72</td>
<td>549.55</td>
<td>11.61%</td>
</tr>
<tr>
<td>2wt%Ag/Cu6Sn5</td>
<td>340/622</td>
<td>416.28</td>
<td>149.17</td>
<td>64.17%</td>
</tr>
<tr>
<td>5% Ag/Cu6Sn5</td>
<td>340/622</td>
<td>260.76</td>
<td>230.84</td>
<td>11.7%</td>
</tr>
<tr>
<td>15% Ag/Cu6Sn5</td>
<td>340/622</td>
<td>140.00</td>
<td>175.67</td>
<td>-25.48%</td>
</tr>
<tr>
<td>Sn</td>
<td>993</td>
<td>211.32</td>
<td>24.66</td>
<td>88.33%</td>
</tr>
</tbody>
</table>

### Table 6: Reduction Potential for Silver Salts

<table>
<thead>
<tr>
<th>Salt</th>
<th>Reduction Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver oxalate</td>
<td>1.5</td>
</tr>
<tr>
<td>Silver ascorbate</td>
<td>2.8</td>
</tr>
<tr>
<td>Silver fumarate</td>
<td>1.0</td>
</tr>
<tr>
<td>Silver succinate</td>
<td>2.0</td>
</tr>
</tbody>
</table>
FIGURES

Figure 1: Structure of Cu₆Sn₅

Figure 2: Structure of Li₂CuSn
Figure 3: Laminates with electrodes punched out

Figure 4: Time Profile for Chinese Graphite in the Voltage Window of 1.5 to 0.01 V
Figure 5: Time Profile for GDR Graphite in the Voltage Window of 2 to 0.01 V

C-GDR Time Profile

Figure 6: Time Profile for 1% Ag/C-GDR in the Voltage Window of 1.5 to 0.01 V

1% Ag/C-GDR Time Profile
Figure 7: Time Profile for 3% Ag/C-GDR in the Voltage Window of 1.5 to 0.01 V

Figure 8: Time Profile for 5% Ag/C-GDR in the Voltage Window of 2 to 0.01 V
Figure 9: Discharge Capacities for C-GDR with no Ag, 1% Ag, 3% Ag, and 5% Ag

Discharge Capacities for C-GDR: Tollens

---

Figure 10: Irreversible Capacities for C-GDR with no Ag, 1% Ag, 3% Ag, and 5% Ag

Irreversible Capacity for C-GDR: Tollens
% Capacity Loss from Cycle 1 to 2
Figure 11: Time Profile for Cu₆Sn₅ in the Voltage Window of 2 to 0 V

Figure 12: Time Profile for Cu₆Sn₅ in the Voltage Window of 2 to 0.2 V
Figure 13: Time Profile for 5% Ag/Cu₆Sn₅ in the Voltage Window of 2 to 0.2 V

5% Ag/Cu₆Sn₅ Time Profile

Figure 14: Time Profile for 15% Ag/Cu₆Sn₅ in the Voltage Window of 2 to 0.2 V

15% Ag/Cu₆Sn₅ Time Profile
Figure 15: Discharge Capacities for Cu₆Sn₅ with no Ag, 5% Ag, and 15% Ag

Discharge Capacities for Cu₆Sn₅: Tollens

Figure 16: Irreversible Capacities for Cu₆Sn₅ with no Ag, 5% Ag, and 15% Ag

Irreversible Capacities for Cu₆Sn₅: Tollens Method
% Capacity Loss from Cycle 1 to 2
Figure 17: Time Profile for Cu6Sn5 with 0.5% AgNO3 in LP40 in the Voltage Window of 2 to 0.01 V

Figure 18: Time Profile for Cu6Sn5 with 4.6% AgClO4 in Gen 3 in the Voltage Window of 2 to 0 V
Figure 19: Discharge Capacities for Cu₆Sn₅ with no Ag, 0.5% AgNO₃ in LP40, and 4.6% AgClO₄ in Gen 3

Discharge Capacities for Cu₆Sn₅: In-situ Deposition

Figure 20: Irreversible Capacities for Cu₆Sn₅ with no Ag, 0.5% AgNO₃ in LP40, and 4.6% AgClO₄ in Gen 3

Irreversible Capacities for Cu₆Sn₅: In-situ Deposition
% Capacity Loss from Cycle 1 to 2
Figure 21: Time Profile for Silver Oxalate – Discharged to 1.0 V

Silver Oxalate Time Profile

Figure 22: Time Profile for 2% Ag/Cu₆Sn₅ in the Voltage Window of 1.5 to 0.01 V

2% Ag/Cu₆Sn₅ Time Profile
Figure 23: Discharge Capacities for Cu₆Sn₅ with no Ag and 2% Ag

Discharge Capacity for Cu₆Sn₅: Physical Mixture

Figure 24: Irreversible Capacities for Cu₆Sn₅ with no Ag and 2% Ag

Irreversible Capacity for Cu₆Sn₅: Physical Mixture
% Capacity Loss from Cycle 1 to 2
Figure 25: Powder X-Ray Diffraction of 1% Ag/C-GDR

1% Ag/C-GDR

Figure 26: Powder X-Ray Diffraction of 1% Ag/Cu_5Sn_5

1% Ag/Cu_5Sn_5
Figure 27: Powder X-Ray Diffraction for Silver Succinate

Silver Succinate

Figure 28: SEM of 5% Ag/Cu₆Sn₅: Ball Milled
Figure 29: SEM of 3% Ag/Cu₆Sn₅: Tollens Method

Figure 30: SEM of 3% Ag/Cu₆Sn₅: Tollens Method
Figure 31: SEM of 1% Ag/Cu₆Sn₅: Tollens Method