



Evaluation of the Electrochemical Properties of Crystalline Copper Antimonide Thin Film Anodes for Lithium Ion Batteries Produced by Single Step Electrodeposition



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ABSTRACT

Electrodeposited crystalline Cu_2Sb thin films are studied to evaluate the use of these electrodes as model systems for studying Cu_2Sb as a lithium ion battery anode material. The films have been characterized with an emphasis on determining the film quality and relating the structure, composition, and morphology to the resulting electrochemical and morphological transformations that occur during electrochemical lithiation and delithiation. It is shown that electrodeposition can produce high quality films that are devoid of major defects and can be used to provide mechanistic insight on the electrochemistry of reversible lithium alloying. The Cu_xSb films show that the fundamental reaction mechanism remains largely unchanged for copper concentrations of $1 > x > 3$. For the first time we show that the copper concentration greatly affects critical criteria for anode materials such as the initial coulombic efficiency and reversible capacity of the electrode material. Voltage limit experiments show that an overpotential is required to remove trapped lithium states. Additional ex-situ experiments reveal that internal strain created during the lithiation process is relieved by buckling, greatly altering the film surface area and geometry, and resulting in the formation of cracks upon delithiation. This process is only semi-reversible, and strained areas remain visible even when discharged outside the voltage window of Cu_2Sb determined by differential capacity plots. The results presented here indicate that these electroplated thin films are useful as analytical tools for showing pathways to improving the performance and fundamental understanding of alloy based lithium-ion battery anodes.

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1. Introduction

Commercial lithium ion batteries are the current leading energy storage device for portable electronics applications due to the exceptionally high energy density they provide. These cells, generally utilizing a LiCoO_2 cathode and a graphite anode separated with an electrolyte consisting of LiPF_6 in organic carbonates, show good capacity retention and a high operating cell voltage [1]. Despite this, the currently used battery architecture has considerable safety concerns due to the flammability of the carbonate electrolyte, the decomposition of LiCoO_2 to produce oxygen, and the formation of lithium dendrites when overcharged

[2]. In order for Li-ion batteries to meet the criteria for next generation technologies such as electric vehicles and aerospace applications, new materials and device architectures are required to provide higher energy density, higher power density, improved safety, and longer cycle life at reduced cost [2,3]. Proposed methods to achieve this include new cell chemistries, such as the lithium-sulfur battery [4] or the lithium-air battery [5,6], and sodium-ion battery [7], as well as the use of non-planar, nanoscale battery architectures [8–11] coupled with novel materials allowing faster kinetics, larger capacities, better cycle life and enhanced safety. Regardless of the approach, new techniques for producing high quality materials with tunable morphology and chemistry are required for next generation battery technology.

The capacity of batteries can be improved by using new electrode materials that reversibly react with a higher number of lithium ions per unit mass or unit volume of the electrode material. For this reason, binary lithium-metal systems have been studied as potential anode materials because of their very high theoretical

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gravimetric and volumetric capacities [12]. Lithium undergoes the electrochemical reaction $x\text{Li} + \text{M} \rightarrow \text{Li}_x\text{M}$ (for $\text{M} = \text{Al}, \text{Mg}, \text{Si}, \text{Sn}, \text{Sb}$), where the amount of lithium incorporated is dependent on the stoichiometry of the final Li_xM phase. These reactions occur in the potential range of 0–1.2 V vs. Li/Li^+ , and with relatively modest voltage hysteresis, and are feasible high energy density anode materials. Despite these advantages, these alloy electrodes cannot typically be used without modification due to the large change in volume accompanying the lithium insertion and desorption process. This causes the active material to pulverize, leading to loss of contact to the electrode, and results in a large capacity fade within only a few cycles. Other issues include the poor electrical conductivity and high brittleness of the lithiated compounds. To overcome these limitations, nanoscale particles and other morphologies have been used, in conjunction with conductive matrixes, which accommodate large volume changes and increase electrical conductivity. Similarly, nanostructured anodes, such as nanowire arrays [13–15] and hollow particles [16], have shown promise for overcoming pulverization by incorporating empty space into the electrode design.

One approach toward mitigating the aforementioned limitations of metal anodes is to incorporate a second inactive metal component M' (for $\text{M}' = \text{Mn}, \text{Ni}, \text{Cu}$, etc.). This second metal acts as a conductive matrix and buffer to volume changes [17–20]. This reduces the energy density of the anode in exchange for reduced pulverization, increased conductivity, and improved mechanical properties. In these systems, the material may undergo one or more processes that are classified as conversion, solid solution, or insertion reactions. The type of reaction, the extent of crystallization of the intermediate, and the final phases present during cycling have been shown to vary substantially based on a number of factors. These include the alloying element, the active material morphology, and the chosen electrochemical conditions. These anode materials and their electrochemistry have recently been reviewed in detail [21].

Among the possible antimony-based materials studied, tetragonal Cu_2Sb has been rigorously investigated due to both the good capacity retention it exhibits during short term cycling and the discovery that the parent structure can be regenerated repeatedly during cycling [22]. The small volume change and structural similarity between the parent compound, intermediate phases, and final Li_3Sb product have been suggested to play a pivotal role in the good performance of this system [17,19]. Electrodes composed of Cu_2Sb have been produced by a variety of methods, such as thin film deposition [23–27], high temperature solid-state techniques [28–31], and chemical reduction [32–35]. Further modification using additives [36], carbon coatings [37], or changing particle morphology [31], which result in both high capacity and long cycle life have been reported.

Electrodeposition has been shown to be capable of producing high quality deposits of Cu_2Sb , either directly [26] or through an annealing step [25]. This technique allows the direct application of the desired material onto a conductive substrate with good electrical contact, without requiring conductive additives or binding agents. Although the feasibility of using Cu_2Sb particulates in traditional porous electrode designs has been thoroughly investigated by Manthiram *et al.* [38–41], improvements in the energy and power density could be achieved by eliminating the need for binder, volume buffer, and conductive additives. The intermetallic Cu_2Sb is of particular interest for this electrode design due to the small relative volume change when compared to anode materials with similar volumetric energy densities based on intermetallics. Some progress has already been made towards developing this type of pure intermetallic electrode by utilizing three dimensional electrode architectures, as has been shown for NiSb [42] and Cu_2Sb [43–45]. A comprehensive understanding of

the mechanism for unsupported Cu_2Sb is critical to the development of this material system as a potentially safer alternative to graphite anodes.

In the present study, we have analyzed crystalline Cu_2Sb deposits produced directly through a room-temperature aqueous electrodeposition without a post-annealing step. This process is environmentally benign and requires substantially lower energy input than traditional solid state and gas phase synthesis methods. Additionally, the reagents used are abundant and inexpensive, giving this method significant commercial potential. Careful analysis of the chemistry of thoroughly characterized binderless thin films is a critical step toward this goal. Although thin films of nominally pure Cu_2Sb films made by electrodeposition have been reported previously, here we show that electrodeposition provides precise control over the composition of the film without annealing, allowing access to copper-deficient Cu_xSb films. More importantly, we have combined characterization methods that couple information about the structure, composition, and morphology of the films with in-depth battery cycling studies. We find that electrodes produced using this system to work best when the particle size is small and when the copper content is lower than the 2:1 necessary to form Cu_2Sb . Ex-situ profilometry and microscopy reveal that the films are ductile but fracture significantly upon repeated cycling, limiting pure and dense Cu_2Sb films to thin thicknesses only. While the electrodeposition method provides a tunable and facile synthetic method, the work described herein informs future directions in providing high quality nanostructures or the incorporation of inactive material to overcome the issue of pulverization and loss of active material.

2. Experimental

The Cu_2Sb thin films were synthesized by electrodeposition between 21–23 °C using a Gamry Reference 3000 potentiostat. Depositions were performed using a copper foil substrate (McMaster Carr, 99.0% Cu), stainless steel counter electrode (McMaster Carr, Alloy 316 mesh), and a saturated calomel (SCE) reference electrode. Copper foils were cleaned using a commercial alkaline cleaning agent (Alconox), followed by rinsing in Millipore water, and subsequently washed in acetone and isopropyl alcohol before drying. Deposition solutions were prepared by first dissolving 25 mM Sb_2O_3 (Sigma-Aldrich, nanopowder, $\geq 99.9\%$) in a solution of 0.40 M citric acid (Sigma-Aldrich, $\geq 99.5\%$) in Millipore water (18.2 $\text{M}\Omega\text{cm}$) by mixing at room temperature for at least 12 hours. Once the Sb_2O_3 was dissolved, 80 mM $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 99.99\%$) was added and the solution was brought to a pH of 6.0 by addition of a concentrated KOH solution. Cyclic voltammetry was performed using a platinum working electrode (2.01 mm^2), platinum mesh counter electrode, and a saturated calomel reference electrode (SCE).

Scanning electron microscopy was performed on a JEOL JSM-6500 F operating at an accelerating voltage of 15 kV and equipped with a Thermo Scientific energy dispersive x-ray system (Noran System Six). Glancing angle x-ray diffraction (GAXRD) was performed using a Bruker D8 Discover using a 1-degree incident angle with a $\text{Cu K}\alpha$ source, soller slit assembly, and a Peltier detector. Ex-situ powder x-ray diffraction (PXRD) patterns were obtained using a Scintag X-2 Advanced Diffraction System equipped with a $\text{Cu K}\alpha$ source and Peltier detector. Optical profilometry surface profiles were obtained on a ZeScope Optical Profiler using a 50x objective lens (31.32x actual magnification) over a 300 μm x 500 μm region.

Electrochemical performance testing was carried out using Arbin BT2000 series battery testers under constant current

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