Single-Bath Electrodeposition of a Combinatorial Library of Binary Cu$_{1-x}$Sn$_x$ Alloys

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Electrodeposition from a single bath in a single run was used to create a combinatorial library of binary Cu-Sn alloys. Electron microprobe and X-ray diffraction studies were used to determine the average stoichiometry and the phases present as a function of position on the substrate foil. The deposited film follows the Cu-Sn phase diagram, except that Cu$_3$Sn$_2$ was observed instead of Cu$_3$Sn. Electrodes with various average stoichiometry were punched from the film and tested as negative electrodes for Li-ion cells. Electrodes taken from the high Sn content area of the electrodeposited film display high capacity (~600 mAh/g) but poor capacity retention with cycling. Electrodes taken from the high Cu content area of the film display reduced capacity (~300 mAh/g) with dramatically improved capacity retention.


Cu-Sn alloys have been proposed as possible anode materials for Li-ion cells. Kepler et al. showed that Cu$_3$Sn$_2$ can react reversibly with lithium for a few tens of cycles. Larcher et al. studied the Li$_x$Cu$_{2y}$Sn$_{3x}$ reaction using in situ X-ray diffraction (XRD). Tamura et al. showed that Cu-Sn alloys could be prepared by electrodepositing pure tin on copper foil, followed by an annealing step. Beattie et al. described by Larcher the electrochemical behavior in lithium cells as the powdered samples described by Larcher et al. Electrodeposited films have the advantage that they could be directly used as electrodes in lithium-ion batteries without further processing.

There are a number of binary intermetallic Cu-Sn phases, and the electrochemical properties of each should be considered. However, some of these phases, like Cu$_3$Sn$_2$ and Cu$_3$Sn, contain little tin so one would expect them to react with little lithium, and hence be relatively "inactive" phases. On the other hand, Mao et al. have shown that it can be advantageous to mix relatively inactive phases like SnFe$_2$C with active phases like Sn$_x$Fe$_y$ in efforts to obtain materials with good capacity retention and acceptable specific capacity. Therefore, we decided to prepare mixed intermetallic phases in the Cu-Sn system.

We decided to prepare Cu-Sn alloys with varying composition by electroplating. Based on our previous work, we believed that a wide range of Cu-Sn alloy compositions could be electrodeposited from a single bath using pulsed deposition in a Hull cell. Alloys prepared using a Hull cell and its variations (i.e., rotating cylindrical Hull, RCH cell) have been discussed in the literature. Our method is similar to ones used in. However, our method is unique because a low frequency on/off pulsed waveform and the geometry of the Hull cell are used to exploit the exchange of deposition Sn by aqueous Cu to achieve a composition and structural spread as a function of position on the substrate. To our knowledge such a novel preparation scheme is a new method in combinatorial materials synthesis.

Figure 1 shows electron microprobe results for a Cu-Sn composition-spread film prepared via electrodeposition in a single run. Starting from the bottom, Sn-rich end of the film, the position in centimeters is plotted vs. the Cu-Sn atomic ratio. The Cu-Sn atomic ratio increases along the length of the film. This shows that a combinatorial library of Cu-Sn alloys has been prepared via electrodeposition. Below, we will describe the preparation method and the behavior of a number of compositions as electrodes for Li-ion cells.

Experimental

Cu-Sn alloys were deposited from a pyrophosphate solution: 36 g/L Sn$_2$P$_2$O$_7$, 135 g/L K$_2$P$_2$O$_7$, 1 g/L Cu$_2$P$_2$O$_7$·3H$_2$O. Without the addition of additives a pyrophosphate bath has poor throwing power. A solution with good throwing power deposits a constant thickness film regardless of macroscopic cathode irregularities. A solution with poor throwing power is needed to obtain varying thickness along the cathode in the Hull cell. The bath was operated at room temperature without agitation.

Deposition was performed in a Hull cell, not "normal" specifications made from polyvinyl chloride (PVC). The cell is 7.5 cm wide. The cathode is inclined at a 51.5° angle with respect to the anode, which is 7.5 cm wide. The closest approach of anode to cathode is 1.0 cm, and the furthest separating distance is 9.0 cm. The cathode is 11.0 cm in length and the cell is 6.9 cm tall. The cell has a volume of approximately 250 mL. A dimensionally stable titanium anode was used.

All films described here were deposited on Ni foil. To ensure minimal contamination of the bath and a clean deposition surface, the Ni foil was pretreated. The foil was wiped with acetone, ethanol, and then methanol. 3M plater’s tape was used to secure the foil to the PVC backing around the immersed edges to prevent deposition on the back of the foil. Note that the platers tape slightly decreases the available area for deposition. The usable area is decreased from 11.0 × 7.5 cm to approximately 10.5 × 7.0 cm. The PVC vessel and anode were also wiped down prior to deposition.

Pulsed deposition was performed using a Keithley 236 source measure unit. A Visual Basic program was written to apply pulsed waveforms using the Keithley. All deposits were performed galvanostatically.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) studies were performed using a JEOL JXA-8200 superprobe with a Noran energy dispersive spectrometer.

XRD measurements were performed using an INEL CPS120 curved position sensitive detector coupled to an X-ray generator equipped with a Cu target X-ray tube. There is a monochromator in the incident beam path that limits the wavelengths striking the sample to Cu Kα. The incident angle of the beam with respect to the sample is about 6°. The detector measures the entire diffraction pattern between scattering angles of 6° and 120° at once. The film sample is placed on an x-y translating stage that allows measurement and move operations to be sequentially programmed. Scans were taken incrementally along the length of the film. To encourage homogeneity of coexisting phases the film was annealed under argon at 200°C for 2 h prior to XRD analysis. The film was not annealed before EDS analysis.

Cu-Sn film samples were tested in Li/Cu-Sn cells for their specific capacity and capacity retention. Standard 2325 (23 mm diam, 2.5 mm thick) coin cell hardware was used. The cells use a polypropylene microporous separator, 1 M LiPF$_6$ dissolved in ethylene carbonate/diethyl carbonate (EC:DEC, 33:67 vol, Mitsubishi Chemical) electrolyte and lithium metal as the negative electrode. All cells were assembled in an argon-filled glove box and tested using constant charge and discharge currents of 30 mA/g.
Electroplating Strategy

In order to prepare the composition-spread library of Cu-Sn alloys, several requirements must be satisfied. First, copper deposits at more positive potentials than tin, so the tin concentration in solution should be much larger than that of copper. Second, the bath should have a poor throwing power (like the pyrophosphate bath we picked) so that the current density varies with the anode and/or cathode distance in the Hull cell. This ensures that the thickness of the deposit varies with position on the substrate foil. Finally, pulsed deposition is used to create the composition spread. A series of on/off pulses are used, because primarily Sn is deposited during the on pulse, and copper from the plating solution ion exchanges with the plated tin during the off pulse according to the reaction \( \text{Cu}^{2+}(aq) + \text{Sn}(s) \rightarrow \text{Cu}(s) + \text{Sn}^{2+}(aq) \). Then, a deposit like that shown schematically in Fig. 2 is created.

Figure 2a shows the layers of tin rich material deposited during the on pulses, whose thickness varies along the length of the substrate electrode, and the layers of ion-exchanged copper deposited during the off pulses, whose thickness is constant along the length of the substrate electrode. In our depositions, the on pulse/off pulse sequence is repeated hundreds of times to deposit a film several micrometers thick. During the on pulse, the layer thickness deposited is estimated to range between 4.7 and 1.3 nm along the length of the substrate. Examinations of the film using small angle X-ray scattering showed that a composition modulated superlattice structure was not formed. Presumably, this is because the copper-rich and tin-rich layers are eliminated by interdiffusion. Therefore, Fig. 2b shows a schematic of the deposited film after the Cu-Sn interdiffusion occurs.

Figure 1 shows that the procedure described above deposits a film where the average stoichiometry varies along the length of the substrate. Each EDS data point in Fig. 1 represents a different number of crystallites being analyzed can vary. This variation could be easily sampled given the proper electrodeposition parameters. Due to lack of control over temperature a structural range would be more difficult to sample.

Electrodeposition was performed at room temperature, however the tabulated phase diagram only extends as low as 100°C. We assume that the phase diagram at 21°C is identical to that at 100°C. All samples in this paper were either prepared and studied at room temperature or were annealed to 200°C under argon. Between 20 and 200°C, the arrow in Fig. 4 passes through five distinct stoichiometric regions: Sn + Cu₆Sn₅, Cu₆Sn₅, Cu₆Sn₃ + Cu₂Sn, C₅Sn, and Cu₂Sn + Cu.

Three positions in the phase diagram (Fig. 4) were chosen for focused study. A high Cu content (4a), a high Sn content (4c), and an intermediate area (4b). According to the phase diagram, sample 4a should correspond to coexisting phases of Cu₆Sn₅ + Cu, sample 4b should correspond to coexisting phases of Cu₆Sn₅ + Cu₂Sn and sample 4c should correspond to coexisting phases of Sn + Cu₆Sn₅. The film was annealed under argon at 200°C for 2 h.
then XRD patterns were taken along the entire length. XRD patterns
taken from the positions labeled 4a-c in Fig. 4 are presented in Fig. 5,
correspondingly labeled 4a-c. XRD patterns taken from pure Sn
and known Cu-Sn alloys are superimposed onto those XRD patterns.
In Fig. 4a, coexisting Cu₃Sn₁, Cu phases are expected from the
phase diagram but they are not observed. Instead, the Cu₄₁Sn₁₁
phase, which does not extend down to room temperature in Fig. 4, is
present. Apparently Cu₄₁Sn₁₁ is favored by the pulsed deposition
process described above, rather than Cu or Cu₃Sn. The peak near
42° in Fig. 4a is thought to arise from a copper phase containing a
small amount of dissolved tin. In Fig. 4b, the Cu₄₁Sn₁₁ phase is
present once again, where Cu₃Sn was expected. The fact that films
fabricated by electrodeposition do not exactly follow the equilibrium
conditions present in a phase diagram at a specified temperature is
not surprising since electrodeposition does not occur at equilibrium
conditions. The Cu₄₁Sn₁₁ phase is in the right stoichiometric range
in the Cu-Sn phase diagram to appear in samples 4a and 4b, but is
not expected at lower temperatures. The Cu₃Sn phase is not ex-
pected at high Cu content, Cu₄₁Sn₁₁ is, therefore the XRD pattern at
position 4b in Fig. 4 should show coexisting Cu₄₁Sn₁₁ and Cu₆Sn₅
phases, as it does in Fig. 5b. Furthermore, at position 4c in Fig. 4,
coexisting Cu₆Sn₅ and Sn is expected, as verified by the diffraction
pattern in Fig. 5c. Electron microprobe results and XRD results
agree with the Cu-Sn phase diagram as long as the Cu₄₁Sn₁₁ phase is
expected at high Cu content.

Figure 6 shows XRD patterns along the length of the film. The Cu content increases from bottom to top. Sn rich phases are
observed at the bottom of the film, while Cu rich phases are observed at the top. Bragg peaks from known phases are indicated.

Li/Cu-Sn coin cells were then constructed from circular elec-
rodes punched from various places on the film. Figure 7 shows

Figure 4. The Cu:Sn phase diagram. The arrow indicates the region of phase
space sampled by the film (Fig. 1) deposited in the Hull cell using on/off
pulsed deposition. Three average compositions labeled 4a, 4b, and 4c are
considered for focused analysis.

Figure 5. XRD patterns of portions of the film corresponding to the posi-
tions (a) 4a, (b) 4b, and (c) 4c. Known Sn and Cu-Sn alloy XRD patterns are
superimposed on the data for comparison.

Figure 6. 20 XRD patterns measured at equal spacings along the length of
the film. The Cu content increases from bottom to top. Sn rich phases are
observed at the bottom of the film, while Cu rich phases are observed at the
top. Bragg peaks from known phases are indicated.
specific capacity vs. cycle number and voltage vs. capacity for five electrodes taken along the length of the film. The Cu content increases from bottom to top. The specific capacity decreases with increasing Cu content with a corresponding increase in capacity retention. Solid dots correspond to discharge capacity while empty dots correspond to recharge capacity.

Figure 7. Voltage vs. capacity and capacity vs. cycle number for five Li/Cu-Sn cells with electrodes taken along the length of the film. The Cu content increases from bottom to top. The specific capacity decreases with increasing Cu content with a corresponding increase in capacity retention. Solid dots correspond to discharge capacity while empty dots correspond to recharge capacity.

Figure 7. Voltage vs. capacity and capacity vs. cycle number for five Li/Cu-Sn cells with electrodes taken along the length of the film. The Cu content increases from bottom to top. The specific capacity decreases with increasing Cu content with a corresponding increase in capacity retention. Solid dots correspond to discharge capacity while empty dots correspond to recharge capacity.

specific capacity vs. cycle number and voltage vs. capacity for five electrodes taken along the length of the film. The Cu content increases from bottom to top. The specific capacity decreases with increasing Cu content with a corresponding increase in capacity retention. Solid dots correspond to discharge capacity while empty dots correspond to recharge capacity.

Conclusions

Using electrodeposition, a combinatorial library of binary Cu$_{1-x}$Sn$_x$ alloys has been successfully deposited from a single bath in a single run. The Cu:Sn atomic ratio varies almost linearly along the length of the film. Electron microprobe and XRD data agree with the Cu-Sn phase diagram except that the high temperature Cu$_4$Sn$_1$ phase was observed in place of Cu$_3$Sn. Electrochemical studies of Li/Cu-Sn cells show that Sn-rich regions of the film exhibit high capacity (~600 mAh/g) but poor capacity retention. Cu-rich compounds exhibit lower capacity (~300 mAh/g) with dramatically improved capacity retention.

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