Masked Electrodeposition of a Composition-Spread Library of Sn-Zn Alloys onto a 64-Channel Combinatorial Cell Plate

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The purpose of this dissertation is to describe a simple and inexpensive method to electrodeposit a composition-spread library of metal alloys (Sn-Zn) onto a lead pattern consisting of 64 individually addressable electrodes. The electrodeposited lead pattern can then be loaded into an electrochemical cell where the 64 unique metal alloy electrodes are tested in parallel for their suitability as advanced negative electrode materials for rechargeable Li-ion batteries. Ninety percent of the Sn-Zn binary composition space is sampled in a single electrodeposition experiment. We show how the power of combinatorial screening techniques can be combined with the simplicity and low cost of masked electrodeposition.

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Combinatorial methods are a powerful tool in the rapid discovery of technologically significant materials. To be effective, combinatorial material science requires two separate but equally important steps: (i) deposition of a composition-spread library of materials, and (ii) expedient, parallel testing of these materials. This paper focuses on step (i) with step (ii) in mind. Typically, thin-film vapor deposition or sputter deposition techniques are used to deposit the composition-spread film of materials. These techniques are complex, expensive, and slow. Here, we show that electrodeposition can also be used to prepare composition-spread libraries of materials. Electrodeposition, unlike other deposition techniques, is simple, inexpensive, and fast. We show that a composition-spread library of binary Sn-Zn alloys can be deposited onto a lead pattern of 64 individually addressable electrodes using a simple, masked electrodeposition technique. After deposition, the lead pattern can be loaded into an electrochemical cell capable of testing the 64 unique metal-alloy electrodes in parallel for their suitability as advanced negative electrode materials for rechargeable Li-ion batteries, hence satisfying the requirements for step (ii). The power of combinatorial deposition and screening techniques is now available to the budget-constrained material scientist.

Experimental

Electrodeposition was performed in a potassium pyrophosphate bath containing hydrated Sn and Zn sulfates: 0.66 M (218 g/L) K2P2O7, 0.013 M (3.2 g/L) SnSO4·5H2O, and 0.30 M (86.4 g/L) ZnSO4·7H2O. Deposition of the composition-spread library of Sn-Zn alloys was performed at room temperature in a homemade, modified Hull cell™ made from polyvinyl chloride (PVC), as shown in Fig. 1. The cell is 9.0 cm long, 6.9 cm tall, and 11.5 cm wide. The working electrode is inclined at a 51.5° angle with respect to the counter electrode. The counter electrode is a plate of pure Zn (99.9% Aldrich). The working electrode consists of a 64-channel Cu lead pattern superimposed onto an 11.4 × 11.4 cm glass slide. Refer to Fig. 2 for a schematic of the lead pattern. The lead pattern is fabricated using sputter deposition and UV photolithography. A detailed description of the lead pattern fabrication method can be found in Ref. 3. The closest approach of counter electrode to working electrode is 1.0 cm, and the furthest separating distance is 9.0 cm. The cell has a volume of approximately 250 mL. Prior to deposition the glass slide, PVC vessel, and counter electrode were wiped with acetone, ethanol, and then methanol.

Except for the electrode pads, the entire glass slide lead pattern was painted with coal-tar epoxy. Before painting, a thin strip of Cu is placed along the top and on either side of the glass slide (relative to the orientation shown Fig. 2), shorting all leads together. One of the thin strips of Cu along the side is extended above the slide, providing a tab where electrical contact to all 64 channels is made. After carefully painting around the electrode pads, the coal-tar epoxy was allowed to dry overnight (−9 to 10 h). The glass slide is positioned in the Hull cell as the working electrode, illustrated in Fig. 1.

For reasons to be discussed below, a piece of punched Cu foil (64 holes in exact alignment with the cell plate shown in Fig. 2) was placed over the coal-tar epoxy painted glass slide. The Cu foil is constructed such that it covers the painted coal-tar epoxy, but not the exposed electrode pads. The Cu foil top layer was placed on the glass slide immediately after coal-tar painting to encourage adhesion.

The holes in the Cu foil overlay had to line up exactly with the position of the pads underneath. The positioning of the punches is very important and could not do be done by eye. A thin piece of Cu foil (~15 × 15 cm) was taped to a piece of letter-sized printer paper and fed through a bubble-jet printer. The same graphics file used to make the masks for photore sist UV exposure (refer to Ref. 3) was used to print the exact positions of the electrode pads onto the Cu foil. The electrode hole pattern was then punched from the foil using an appropriately sized hole punch. The overlying Cu foil and underlying electrode lead pattern were then shorted together. As far as the electrodeposition process is concerned, the lead pattern and overlying punched Cu foil act as a single film of Cu foil. The masked lead pattern with overlying punched Cu foil is then placed in the working electrode position as shown in Fig. 1. A current of 100 mA was applied to the cell for 6.28 h. The result is a composition-spread film of Sn-Zn alloys with a thickness gradient between ~1 and 4 μm. The film is thickest at the Sn-rich end and thinnest at the Zn-rich end. Refer to Ref. 4 for a detailed description of the deposition process and film properties.

After deposition the punched Cu foil was removed and the coal-tar epoxy washed away using acetone. If the coal-tar epoxy was left to cure longer than ~9–10 h, it could not be easily removed using acetone. It was found that adding more resin and less hardener than suggested by the preparation instructions resulted in a film that was easily removed and successfully protected the lead pattern during deposition. Approximately ten times less hardener was used than suggested by the preparation instructions.

A Keithley 236 source-measure unit was used in galvanostatic mode to electrodeposit the Sn-Zn alloys.

Energy dispersive spectroscopy (EDS) studies were performed...
using a JEOL JXA-8200 Superprobe with five wavelength dispersive spectrometers to determine composition as a function of position on the electrodeposited films.

Discussion

The combinatorial material science infrastructure at Dalhousie University has grown significantly since its inception in 2000. One example of this infrastructure is the development of a 64-channel combinatorial electrochemical cell (combi-cell) for testing composition-spread libraries of metal-alloy negative electrodes for use in Li-ion rechargeable batteries. A detailed description of the 64 channel combi-cell can be found in Ref. 3.

The combi-cell is constructed in steps. The working electrode is a glass slide with the electrode lead pattern shown in Fig. 2. The positions of the electrode pads are staggered to sample the largest range of binary composition space possible with minimal compositional variation between electrodes. Test negative-electrode materials are deposited in a way such that there is a smooth composition spread between adjacent electrodes. For example, electrode no. 1 may consist of Zn0.9Sn0.1, while the adjacent electrode, no. 2, is Zn0.8Sn0.2. This way, the performance of electrode materials with similar compositions can be compared quickly.

Recently, it has been shown that composition-spread libraries of binary and ternary alloys can be prepared using the economical method of electrodeposition. The method is sometimes referred to as combinatorial electrodeposition. Given the success of the 64-channel electrochemical cell (combi-cell) and combinatorial electrodeposition, an attempt was made to combine the two methods to provide a powerful yet economical method for rapid screening of negative-electrode materials.

Electrodeposition onto the 64-channel lead pattern presented numerous challenges. To be successful the masking technique had to satisfy two criteria: (i) easily removed after deposition without damaging the underlying lead pattern, and (ii) capable of protecting the lead pattern during deposition. Coal-tar epoxy satisfied both these requirements; refer to the Experimental section for a description of the coal-tar painting technique.

After painting and drying the coal-tar epoxy painted electrode pattern was used as the working electrode (as shown in Fig. 1). The configuration shown in Fig. 1 has been used before to fabricate composition-spread libraries of Cu-Sn, Cu-Zn, and Cu-Sn-Zn alloys. Reference 4 is particularly relevant. The deposition technique used in Ref. 4 is very similar to the technique used here. In Ref. 4 there is a detailed discussion on the theoretical and experimental analysis of the electrodeposited film, emphasizing current density, mass, thickness, and compositional distribution. Similar results in compositional variation (compared to Ref. 4) were expected because similar techniques were used. The bath chemistry, electrochemical cell, deposition time, and current density were all the same; the only difference was electrode area. Unfortunately, compositional variation was not achieved. Here’s why: in Ref. 4, a relatively large electrode area was used, ~132 cm², and the deposition current was 100 mA, corresponding to a current density of 0.75 mA/cm². The electroplating bath is rich in Zn and poor in Sn, which preferentially deposits over Zn. The combination of relatively large current density and low Sn concentration causes Sn to be deposited at its limiting current density. If Sn is deposited at its limiting current density, then low current densities will result in Sn-rich alloys and high current densities will result in Zn-rich alloys. In a Hull cell, where current density varies as a function of position, compositional variation of Sn-Zn alloys as a function of position is achieved.

Now, consider the coal-tar epoxy painted lead pattern (without the overlaid punched Cu foil) which has a relatively small area, ~13.2 cm². Given the same current density used in Ref. 4 (0.75 mA/cm²), the deposition current is 10 mA, 10 times less than the current used in Ref. 4. Given equal deposition times, much less metal is deposited/consumed compared to Ref. 4. Because less metal is being consumed, there are more metal ions left in solution to replace those being consumed. Hence, Sn may not be deposited at its limiting current density. The argument is especially compelling when the geometry of the coal-tar painted lead pattern is considered. The electrode pads are arranged in a grid and separated by a well-defined distance. While Sn ions directly above the electrode pads are consumed, there are more metal ions left in solution to replace those being consumed. The area around the electrode pads acts as an “extra” source of Sn ions. This extra source of Sn actively replaces Sn as it is consumed at the electrode and Sn is not deposited at its limiting current density (as it was in Ref. 4). Because Sn is deposited below its limiting current density, and Sn preferentially deposits over Zn, no Zn is deposited. This was observed experimentally. Two factors collaborate to prevent Sn deposition at its limiting current density: (i) less Sn is consumed so the overall change in concentration is less (compared to Ref. 4), and (ii) local variations in Sn concentration are reduced due to the influence of neighboring areas where Sn is not consumed.

In Ref. 7 it is shown that the characteristic length for mass trans-
port corresponds to the thickness of the diffusion layer, typically on the order of a few micrometers. A stagnant diffusion layer is assumed to exist near the electrode, and mass transport proceeds by diffusion and migration only. Using this argument, extra Sn ions from the area surrounding the electrode pads are too far away and would not have time to diffuse in and replace those being consumed. In Ref. 7 it is also noted that convection determines the thickness of the stagnant diffusion layer; the more convection the thicker the diffusion layer. At the current densities used here (0.75 mA/cm²) there was extensive hydrogen evolution. Hydrogen evolution results in local mixing of the electrolyte. This mixing causes Sn ions from the surrounding coal-tar painted area to wash over the electrode pad, replacing Sn ions consumed during deposition. Relative to Ref. 7, mixing results in convention and a thicker diffusion layer. The thicker the diffusion layer the more important the presence of extra Sn ions becomes. Because Sn is constantly replaced by the extensive mixing and thicker diffusion layer Sn is not deposited at its limiting current, density and compositional variations are not observed.

Several options were considered to overcome these problems. Given the previous success with a Sn-Zn pyrophosphate bath and a large surface area working electrode, it was decided that increasing the available deposition area should encourage compositional variation. A piece of punched Cu foil was placed over the coal tar to increase the surface area. The punch pattern on the Cu foil exactly lined up with the position of the electrode pads (Fig. 2). Refer to the Experimental section for a discussion on how the complicated punch pattern was accurately made in the Cu foil.

The final electrodeposited lead pattern is presented in Fig. 3. Figure 3 emphasizes that electrodeposition of test negative electrode materials occurred only on the electrode pads, and not on the lead pattern. Furthermore, compositional variation was successfully achieved, represented by the color gradient on the electrode pads from light gray (Sn rich) to black (Zn rich).

EDS measurements were performed on the punched Cu foil after electrodeposition and removal from the patterned glass slide. Numerous measurements were made along the left-hand side of the film where no punches were removed (e.g., left-hand side of Fig. 3). The results are presented in Fig. 4.

Electrodeposition was highly successful in sampling a large region of composition space. Approximately 90% of the Sn-Zn binary composition space was sampled on one combi-cell plate. Individual compositions are addressable by the lead pattern. Further studies will obviously involve testing the electrodeposited negative electrode materials in a 64-channel electrochemical cell. It is our hope that others involved in combinatorial electrodeposition adopt this simple method of preparing discrete compositions on individual electrodes from a single plating bath using a single current supply connected simultaneously to all electrodes.

Conclusion

Masked combinatorial electrodeposition was successfully performed on an individually addressable 64-channel lead pattern. Ninety percent of Sn-Zn composition space was sampled in a single experiment involving a single bath and a single current supply connected simultaneously to all 64 electrodes. When loaded into the electrochemical combi-cell all 64 electrode materials can be tested in parallel. Combinatorial electrodeposition and parallel electrochemical screening techniques are combined to provide a simple, inexpensive method for the rapid discovery of technologically significant electrode materials.

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References