Nanostructured Lithium-Aluminum Alloy Electrodes for Lithium-Ion Batteries

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Electrodeposited aluminum films and template-synthesized aluminum nanorods are examined as negative electrodes for lithium-ion batteries. The lithium-aluminum alloying reaction is observed electrochemically with cyclic voltammetry and galvanostatic cycling in lithium half-cells. The electrodeposition reaction is shown to have high faradaic efficiency, and electrodeposited aluminum films reach theoretical capacity for the formation of LiAl (1 Ah/g). The performance of electrodeposited aluminum films is dependent on film thickness, with thicker films exhibiting better cycling behavior. The same trend is shown for electron-beam deposited aluminum films, suggesting that aluminum film thickness is the major determinant in electrochemical performance regardless of deposition technique. Synthesis of aluminum nanorod arrays on stainless steel substrates is demonstrated using electrodeposition into anodic aluminum oxide templates followed by template dissolution. Unlike nanostructures of other lithium-alloying materials, the electrochemical performance of these aluminum nanorod arrays is worse than that of bulk aluminum.

Introduction and Background

Lithium alloys have gained recent prominence as candidate materials for the negative electrode in lithium-ion batteries (1). The advantage of lithium-alloy electrodes is their high theoretical capacity (two to ten times that of graphite), but they face major obstacles to commercialization because of poor cycling. The failure mechanism most often cited for lithium-alloy electrodes is fracture and pulverization of the active material due to large volume changes. Thus, nanostructured lithium-alloying electrodes have become a focus of research because materials with smaller dimensions can more easily accommodate the large strains. There is a continued need for fundamental understanding of nanoscale effects in lithium-alloy electrodes, specifically the interdependence of particle size, spatial arrangement, and electrochemical behavior.

Aluminum electrochemically alloys with lithium (2) but has been far less explored than silicon and tin. Electrochemical alloying of lithium and aluminum at room temperature produces only LiAl (3), which has a theoretical capacity of 990 mAh g\(^{-1}\). This is on par with that of Li\(_{22}\)Sn\(_5\) but significantly lower than that of Li\(_{22}\)Si\(_5\), each of which undergoes at least three phase transitions to reach full lithiation. Aluminum has the advantage of only one phase transition during lithium insertion, resulting in a single, flat voltage profile. Thus, the LiAl anode may be simpler to characterize and more appropriate for fundamental studies of electrochemical alloying and nanoscale effects. Aluminum is also
beneficial because of its low cost, wide availability as a recycled material, and ability to be electrodeposited. Only a few previous studies have demonstrated the performance of nanoscale aluminum in lithium-alloying electrodes (3-6).

A common method for preparing nanostructured lithium-ion electrodes with controlled dimensions is to deposit the active material onto an array of copper nanorods acting as current collectors. The nanorod array architecture provides enhanced electron conduction and free volume for material expansion upon lithium insertion. Nanorod arrays are typically synthesized by electrodeposition of the material of interest into a template, followed by chemical dissolution of the template. In the original example of this approach, high rate capability and cycle life were achieved with Fe₃O₄, an insulating material for lithium-ion negative electrodes (7). The approach has also been successfully demonstrated with Ni₃Sn₄ (8) and pure tin (9) as active materials. The study of active materials themselves (rather than current collectors) as template-synthesized nanorod arrays is largely absent from the literature. The control over nanorod dimensions and spacing offered by template synthesis would be beneficial in the study of nanosize effects in lithium-alloy electrodes. The ability of aluminum to be electrodeposited enables the creation of aluminum nanorod arrays by template synthesis.

Presented here is the room-temperature electrochemical alloying of aluminum films with lithium and the subsequent cycling of such films. A comparison is made between aluminum films formed by electrodeposition and by electron-beam deposition. The effect of film thickness on cycling is examined. Electrodeposition is then utilized in the template synthesis of aluminum nanorod arrays. Preliminary electrochemical cycling performance of such nanostructures is also presented here. Significant size effects and distinct behavior (compared to other lithium-alloy electrodes) were observed.

Experimental Methods

Substrate Preparation

Copper substrates (0.25 mm thick, 99.9985% purity, Alfa Aesar) and stainless steel 316 substrates (McMaster-Carr) were polished with emory paper, 1-µm Al₂O₃ slurry, and 0.05-µm Al₂O₃ slurry and were cleaned by sonication in ethanol for 15 minutes. Copper substrates were then dipped in concentrated sulfuric acid and rinsed with de-ionized water. All substrates were stored in a helium-filled dry box.

Aluminum Electrodeposition

Aluminum films were formed by electrodeposition on copper substrates. The procedure otherwise followed that of Jiang et al (10). The aluminum electrodeposition solution was prepared by slow addition of anhydrous aluminum chloride (99%, Acros) to 1-ethyl-3-methylimidazolium chloride (95%, Sigma-Aldrich) in a helium-filled dry box. The mixing is highly exothermic and must be done slowly to avoid solvent decomposition. A copper disk of 3/8-inch diameter with a masked backside was used as the working electrode. A three-electrode cell consisting of the working electrode, an aluminum foil (99.99%, Alfa Aesar) counter electrode, and an aluminum wire (99.999%) reference electrode was assembled in the dry box. The electrodeposition solution was heated to 60°C.
for all deposition experiments. Galvanostatic deposition was performed at various current densities using a PAR 273A or Solartron 1286 potentiostat/galvanostat. Electrodeposited aluminum samples were removed from the dry box and rinsed in acetone and methanol before further use. Energy-dispersive x-ray spectroscopy (EDAX Genesis) confirmed that the samples consisted mainly of aluminum with traces of oxygen and chlorine.

**Electron-Beam Deposition of Aluminum**

Aluminum films were formed by electron-beam deposition on copper substrates using a custom-built CVC E-beam evaporator with a 10-kV Airco Temescal CV-8 power supply. Chamber pressure during deposition was less than $5 \times 10^{-7}$ torr. Aluminum film thickness was measured *ex situ* with profilometry.

**Aluminum Nanorod Synthesis**

Template synthesis of aluminum nanorods was performed with variations of the procedures of Taberna et al. (7) and Perre et al (11). Commercial anodic aluminum oxide (AAO) templates with nominal pore diameter of 0.2 µm (Whatman Anodisc) were used as received. The electrodeposition cell was assembled by sandwiching a stainless steel substrate (3/8-inch diameter disk), Anodisc template, two pieces of cellulose filter paper (Whatman), and an aluminum counterelectrode (3/8-inch diameter disk). The assembly was clamped together and suspended above a pool of aluminum electrodeposition solution (see above) in the dry box. The edge of the filter paper was placed in contact with the solution so that the solution wicked up to soak the filter paper and template. Galvanostatic deposition was then performed at 0.5 mA/cm² for 1 hour. This initial deposition step anchored the template onto the substrate. The substrate-template assembly was rinsed in acetonitrile, and further deposition was performed in a three-electrode cell at 60°C and 5 mA/cm². The sample was then removed from the dry box and rinsed in acetone and methanol. The template was removed by immersing the sample in an aqueous solution of 1.8 wt% CrO₃ and 6 wt% H₃PO₄ at 60°C for two hours.

**Lithium Half-Cell Assembly and Testing**

Lithium half-cells were assembled in Swagelok-type fixtures in the dry box. The cells consisted of a working electrode (Al film or nanorods on substrate disk), glass microfiber separators (Whatman GF/D) soaked with electrolyte solution, and a lithium foil counter electrode (FMC). The electrolyte solution was 1 M LiPF₆ in a 1:1 mixture (by volume) of ethylene carbonate and dimethyl carbonate (Novolyte). Cyclic voltammetry and galvanostatic cycling were performed on the cells at room temperature with a PAR 273A or Solartron 1286 potentiostat/galvanostat. Voltage limits for cycling were 10 mV and 1.0 V. All quoted potentials are relative to Li/Li⁺.
Results and Discussion

Electrodeposited Aluminum Films

Aluminum films formed by electrodeposition exhibit good adhesion to the copper substrate and have a smooth, light-gray appearance. Cyclic voltammetry was performed on lithium half-cells with aluminum working electrodes to observe the electrochemical alloying-dealloying of aluminum with lithium. The CV curves for the first and tenth cycles of an electrodeposited aluminum film (~1 µm thick) are shown in Figure 1. There is one prominent peak in the lithiation sweep (negative current), between 0.1 and 0.2 V, and one prominent peak in the delithiation sweep, near 0.5 V. These peaks correspond to alloying and dealloying reaction, respectively. The additional small oxidation peak at 0.3 V and the large peak separation are as yet unexplained, but all of these same features were observed in a previous study that used sputtered aluminum films (3). Thus, the basic characteristics of this electrochemical alloying reaction at room temperature are the same for electrodeposited films as for films formed by sputtering. Also observed in Figure 1 is the large reduction in peak height after 10 cycles, likely due to electrode pulverization upon cycling as in other lithium-alloy electrodes.

![Cyclic voltammogram (50 µV/s) of an aluminum/lithium cell. The working electrode is an aluminum film that was formed by electrodeposition at 1 mA/cm² for 1 hour, resulting in an average film thickness of 1 µm.](image)

The potential profile of the first galvanostatic cycle of an aluminum/lithium cell with a thick (~5 µm) electrodeposited Al film is shown in Figure 2. In agreement with the cyclic voltammetry, there is a prominent lithiation plateau below 0.2 V and a prominent delithiation plateau near 0.5 V. The gravimetric capacity (in mAh per gram of aluminum) in Figure 2 was calculated in one of two ways. For the solid line, the aluminum mass was measured with a laboratory balance by weighing the substrate before and after deposition. For the dotted line, the mass of aluminum was calculated from the coulombs passed during aluminum deposition. As shown, the values are in close agreement (less
than 3% difference), indicating high faradaic efficiency in the electrodeposition reaction. Thus, coulometry can be used to calculate the mass of deposited aluminum, which is necessary for thinner films that are too light to be measured by the laboratory balance. All subsequent gravimetric capacities reported here for electrodeposited films were calculated with aluminum mass from coulometry. The first lithiation of the film shown in Figure 2 has a capacity of 977 mAh/g, close to the theoretical capacity of 993 mAh/g.

Figure 2. First galvanostatic cycle (1C rate, i.e. 990 mA/g) of an aluminum/lithium cell. The working electrode is an aluminum film that was formed by electrodeposition at 5 mA/cm² for 1 hour, resulting in an average film thickness of 5 µm.

The voltage profile of the first galvanostatic lithiation of electrodeposited aluminum films of varying thickness is shown in Figure 3. The average thickness of films is calculated from the coulometric charge of the electrodeposition and the density of bulk aluminum. The initial sloping voltage observed in Figure 3 is more significant for thinner films, which was also observed in one previous study (3). Because of the strong dependence of this portion of the curve on film thickness and the fact that the applied current is proportional to the total amount of lithium (“1C” rate), this sloping voltage is attributed to a surface reaction. It is far less significant in subsequent cycles, and it is likely related to electrolyte breakdown and solid-electrolyte interphase (SEI) formation. In the case of the two thicker films, the flat portion of the voltage curves span approximately one hour, indicating that these films reached theoretical lithiation capacity. For the 0.2-µm film, the voltage profile is dominated by the surface reaction, and the formation of LiAl does not appear to reach theoretical capacity. SEM images of these thinnest “films” reveal that they are not continuous films but separate nucleating regions with bare copper exposed on much of the substrate. The higher surface area of such morphology makes the sample more susceptible to oxidation, which may explain the inability to reach theoretical capacity. An alternative explanation is that the Faradaic efficiency of aluminum deposition at this low current density is not close to 100%, as it is for thicker films, thus resulting in an overestimate of the aluminum mass.
The cycling performance of electrodeposited aluminum films is highly dependent on film thickness. In general, the lithiation capacity of each cycle closely matches the delithiation capacity of the previous cycle. However, the delithiation capacity is usually only a fraction of the previous lithiation capacity, resulting in significant capacity decreases within the first few cycles. Voltage profiles of two different electrodeposited aluminum samples during galvanostatic cycling are shown in Figure 4. For the film of 0.2-µm average thickness, the voltage plateaus corresponding to the alloying and de-alloying reactions are barely detectable after only few cycles. The 5-µm film, while also decreasing in capacity, continues to exhibit prominent voltage plateaus after more than 10 cycles. Galvanostatic cycling performance of films of five different thicknesses is shown in Figure 5. As shown, thicker films exhibit better cycling performance. This is in contrast to the conventional wisdom that lithium-alloy electrodes with smaller dimensions can more easily accommodate large volume changes and thus exhibit better cycling performance (12-14). To our knowledge, the dependence of LiAl cycling performance on aluminum film thickness has not previously been studied, and the reason for the unexpected trend is as yet unknown. SEM images of the 2-µm electrodeposited Al film before and after cycling is shown in Figure 6. Upon cycling, the film develops a three-dimensional, highly porous structure that appears to retain some continuity. This is also in contrast to previous reports of lithium-alloy films, which typically appear as flat film separated into discrete platelets after cycling (6, 12).
Figure 4. Voltage profiles of electrodeposited aluminum samples during galvanostatic cycling at 1C rate in lithium half-cells. Estimated average thickness of aluminum samples: (a) 0.2 µm and (b) 5 µm.

Figure 5. Charge (i.e. delithiation) capacity of aluminum samples of varying thickness. Aluminum films were formed by electrodeposition for 1 hour at the current density specified in legend. Approximate film thickness (calculated from coulometry and aluminum bulk density) also indicated in legend.
E-Beam Deposited Aluminum Films

The use of e-beam evaporation for film deposition produces smooth, continuous aluminum films that adhere well to the copper substrate. Films of two different thicknesses, 0.18 µm and 0.85 µm, were produced. Aluminum mass loading is estimated from these values and the bulk density of aluminum (2.7 g/cm³). The electrochemical performance in lithium half-cells largely agrees with that of electrodeposited aluminum samples. Voltage profiles of the two samples during galvanostatic cycling at 1C are shown in Figure 7. As with the electrodeposited samples, the initial sloping voltage profile is much more prominent for the thinner film and is only significant in the first cycle. The voltage plateaus corresponding to LiAl formation and deformation in the thinner film disappear after only five cycles, and cycling of the thicker film is much better. One notable difference is that the 0.18-µm e-beam film reaches theoretical capacity in the first lithiation, evidenced by the one-hour span of the flat voltage plateau in Figure 7. This is in contrast to the 0.2-µm electrodeposited film, which has discontinuous morphology and does not reach full capacity. Thus, film smoothness or continuity may have a significant effect on electrochemical performance, at least in the initial lithiation and cycling.

Figure 6. SEM images of a ~2-µm thick electrodeposited Al film (a) before and (b) after 25 galvanostatic cycles at 1C rate (990 mA/g) in a lithium half-cell.
A comparison between electrodeposited and e-beam deposited aluminum samples is shown in Figure 8. The charge (delithiation) capacity is plotted for films of two different thicknesses. With each deposition method, the thicker films exhibit better cycling performance. Samples of similar thickness made by different deposition methods exhibit similar cycling behavior. Thus, the thickness of aluminum films may be the major determining factor in lithium-cycling performance, regardless of deposition method or morphology. For a given sample thickness, there are slight differences between deposition methods, and it is to be determined whether the differences are statistically significant. SEM images of ~1-µm samples after 25 cycles are shown in Figure 9. Both films have similar appearance, showing a granular, three-dimensional texture. This is further evidence that film thickness is the determining factor in ultimate performance. The results shown in Figures 8 and 9 also confirm that electrodeposition is an effective method for synthesizing aluminum structures for use in lithium-ion cells, the results being on par with other aluminum-deposition methods (3, 6). The use of electrodeposition enables the synthesis of new types of aluminum structures such as conformal coatings and nanostructures.
Figure 8. Cycling performance comparison of electrodeposited and e-beam deposited aluminum samples in lithium half-cells. Galvanostatic cycling at 1C rate, charge (i.e. lithiation) capacity plotted.

Figure 9. SEM images of ~1-µm thick Al films after 25 galvanostatic cycles at 1C rate in lithium half-cells. Al films formed by (a) electrodeposition and (b) e-beam deposition.

Aluminum Nanorods

Aluminum nanorod arrays on aluminum substrates were previously reported, synthesized by electrodeposition into AAO templates (11). In the present report, aluminum cannot be used as a substrate because it, along with the nanorods, would alloy with lithium during cycling. A substrate that is electrochemically inactive in the lithium half-cell must be used. Aluminum nanorod arrays were initially synthesized on copper substrates, but the samples were poor and irreproducible. This was due to the corrosion of copper in the chromic/phosphoric acid solution used to dissolve the AAO templates. Nanorod arrays were successfully synthesized on stainless steel substrates, and SEM images are shown in Figure 10. The diameter of nanowires is 200-300 nm, and the length is 5-20 µm. From our observations, adhesion of electrodeposited aluminum on stainless steel is
not as good as on copper. Nevertheless, the nanorod arrays on stainless steel were able to be cycled in lithium half-cells, presumably undergoing alloying and dealloying as with the aluminum films. The voltage profile for galvanostatic cycling of an Al nanorod array is shown in Figure 11. One significant difference from the cycling of aluminum films is that the voltage profile here is sloping, although it does begin at the same characteristic voltage. The first lithiation sweep reached 630 mAh/g, falling short of the theoretical capacity, and subsequent cycling is poor. In Figure 12, this cycling performance is compared to that of electrodeposited aluminum films. The capacity vs. cycle number of aluminum nanorods is close to that of the thinnest electrodeposited sample. The similarity in performance is not surprising given that the average thickness of that film is roughly the same as the diameter of the nanorods.

Figure 10. SEM images of aluminum nanorod array synthesized by electrodeposition into AAO template. (a) top view; (b) side view.

Figure 11. Voltage profile of aluminum nanorod array during galvanostatic cycling at 1C rate in lithium half-cell.
Figure 12. Cycling performance comparison of electrodeposited aluminum films and aluminum nanorod array in lithium half-cells. Galvanostatic cycling at 1C rate, charge (i.e. lithiation) capacity plotted.

The sloping voltage profile and poor cycling of aluminum nanorods observed here is in agreement with the only two other known reports of aluminum nanoparticles in lithium half-cells (4, 5). This is in contrast to reports of other submicron and nanoscale lithium-alloy electrodes. Nanorods and nanowires of SnO$_2$ (15), Sn (16), and Si (17, 18) have all exhibited superior performance to their bulk counterparts. It is possible that, in the work presented here, poor adhesion with the stainless steel substrate is partially responsible for the observed performance. However, the combined results of this and previous studies suggest there is a fundamental difference between aluminum and other lithium-alloying materials in terms of size effects and electrochemical performance. Further study of lithium-aluminum alloy electrodes may elucidate the reason for this difference.

Conclusion

As demonstrated here, electrodeposited aluminum films and nanorods electrochemically alloy with lithium at room temperature. The formation of a single alloy, LiAl, with a flat voltage profile allows for distinct separation of surface reaction and bulk alloying reaction. With the exception of the thinnest sample, electrodeposited aluminum films reach theoretical capacity (990 mAh/g to form LiAl). Subsequent cycling shows significant decreases in capacity in the first few cycles and with continued cycling. Cycling is strongly dependent on film thickness, with thicker films exhibiting better performance. Also demonstrated here is that e-beam deposited aluminum films exhibit similar electrochemical performance. SEM images show that cycled films (electrodeposited and e-beam deposited) have a three-dimensional, porous structure. Arrays of aluminum nanorods with 200–300-nm diameter exhibit cycling performance on par with that of 200-nm aluminum films. All of the above observations are in contrast to reports of other lithium-alloying electrodes (e.g. tin and silicon), which typically show improved performance at the submicron and nano scale. If aluminum is to be considered as a viable candidate for
negative electrodes in lithium-ion batteries, a much greater understanding of its electrochemical performance is needed.

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