

Underpotential Deposition of Lithium on Aluminum in Ultrahigh-Vacuum Environments

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The electrochemical properties of clean aluminum in LiClO₄(PEO) solutions have been investigated in ultrahigh vacuum using as electrodes both foils and thin films vapor deposited on boron-doped diamond (BDD) layers supported on Si substrates. Voltammetric scans recorded at temperatures of about 55 °C yielded a set of deposition/stripping peaks at potentials positive to the onset of Li/Al alloy formation, attributed to Li underpotential deposition on Al. The positions of these peaks were found to be in relatively good agreement with those predicted by Gerischer–Kolb's work function correlation, as well as with recent theoretical calculations reported by Lehnert and Schmickler. In the case of Al films supported on BDD/Si, the charge under the stripping peak obtained after polarizing the Al electrode at potentials slightly positive to Li bulk deposition was found to increase with the film thickness. Further optimization of this type of experiments, by using, for example, a quartz crystal microbalance to determine the actual amount of Al deposited on the BDD/Si substrate, will make it possible to measure the stoichiometry of the alloy as a function of the applied potential.

Introduction

Comparative studies of atomic and molecular adsorption at solid/vacuum and solid/liquid interfaces can provide much needed insight into the extent to which the physicochemical properties of adsorbates are modified by the presence of a second condensed phase, including the effects of externally applied electric fields. Along with CO adsorption on single-crystal metal surfaces,¹ metals deposited on host metal surfaces at sub-monolayer coverages may be regarded as archetypical systems of potentially extraordinary value in establishing such correlations. Much of the interest in the electrochemical area has focused on adsorbate/substrate systems of the metal/metal type in which the adsorbate in bulk form has a lower work function than the underlying substrate. Under such conditions, the adsorption/charge-transfer reaction often occurs at potentials more positive than those predicted by bulk Nernstian thermodynamics. This amply documented phenomenon, known as underpotential deposition (UPD),² has received widespread attention in the electrochemical area, due in part to the electrocatalytic properties some of these interfaces display for processes of relevance to energy generation and industrial electrosynthesis.

Recent experiments performed in our laboratories have shown that a variety of poly(ethylene oxide) (PEO) electrolyte salt solutions display remarkably low vapor pressure, even in ultrahigh vacuum (UHV),³ opening new prospects for investigating various aspects of UPD of highly reactive metals, such as lithium and sodium, under conditions which virtually eliminate problems associated with impurities both on the electrode surface and in the solution. Implementation of this novel strategy has already yielded interesting information regarding the UPD of Li on Au⁴ and Ni⁵ and the mechanism of

Li nucleation on foreign substrates,^{3,5} allowing in some cases comparisons to be made with the behavior of Li adsorbed by vapor deposition techniques on the same metal surfaces in UHV.⁶

This paper examines the UPD of lithium on Al foil and on Al thin films vapor deposited on electronically conductive boron-doped diamond (BDD) substrates. These studies were prompted by the rather recent theoretical calculations of Schmickler and Lehnert,^{7,8} which predict Li and Na UPD shifts on low-index Al single-crystal surfaces, and also, from a more technological viewpoint, by the possibility of using Al as a Li storage matrix in battery applications.^{9–18} The use of BDD as a substrate appears especially advantageous, as its extraordinary lack of chemical and electrochemical reactivity may enable *exhaustive* alloy formation to be investigated in the virtual absence of interfacial contributions associated with the underlying substrate.^{19,20}

Experimental Section

All measurements were performed in a Varian UHV chamber (base pressure 2×10^{-8} Pa) coupled to a UHV-compatible antechamber, which is separately pumped by both a turbomolecular pump and a small ion pump (15 L/s). The antechamber is equipped with an array of magnetically coupled manipulators involved in the transfer of specimens (including the Li counter/reference [C/R]/PEO solution assembly) in to and out of the main UHV chamber. Auger electron spectroscopy (AES) data were acquired using a single-pass cylindrical mirror analyzer (CMA, Varian 981-2607) with an integral electron gun. Experiments were conducted using as working electrodes an Al foil (Alfa, 0.13 mm thick, m5N in purity), cleaned by a series of Ar⁺ (600 eV) sputtering and annealing cycles (up to 600 °C), or Al films vapor deposited onto BDD supported on silicon wafers. Some BDD samples were obtained from a commercial

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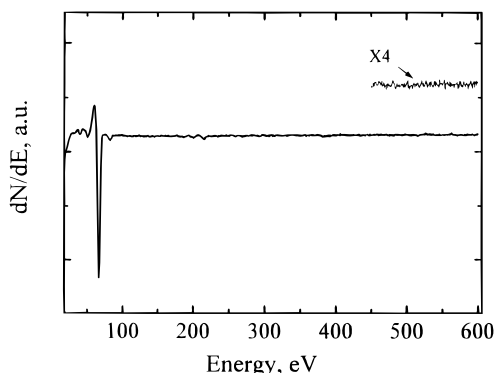


Figure 1. Auger electron spectra of a clean Al foil prepared by the methods described in the Experimental Section. The peaks at 200 and 215 eV are attributed to Ar embedded into the lattice during sputtering. Spectra obtained at higher sensitivity in the range 450–600 eV (see inset) show no trace of oxygen at 505 eV.

source (General Vacuum, Cleveland, OH), while others were prepared in our laboratories.²¹

Aluminum films were produced by resistively heating an aluminum wire (Alfa, m5N, 0.5 mm in diameter) wound around a triply braided tungsten filament.²² Although the thickness of these films could be controlled by adjusting the current and time of deposition, no calibration was attempted in these preliminary studies; hence, the amounts of Al estimated from the relative magnitudes of the Al and C AES signals may be regarded as largely qualitative.

Various details regarding the mounting of the BDD specimens on the sample holder, the procedures used for the heating and temperature control of the cell and for the in situ pre-electrolysis of the PEO(LiClO₄) films, and other experimental considerations have been described in previous publications.^{5,19,20} For studies involving Al/BDD/Si electrodes, however, the PEO(LiClO₄) solution was pre-electrolyzed, using a Ni foil as the auxiliary electrode, and the entire assembly retracted and isolated into the antechamber at reduced pressures before aluminum deposition. Once the Al film had been prepared and its surface composition assayed with AES, the Li[C/R]/PEO(LiClO₄) assembly was immediately brought back into the UHV chamber and placed in contact with the Al/BDD/Si electrode.

Cyclic voltammetry experiments were carried out at temperatures in the range 55–60 °C at a scan rate of 5 mV/s using instrumentation described elsewhere.⁶ All potentials are reported with respect to the Li[C/R] electrode.

BDD surfaces were imaged in air with a Nanoscope II atomic force microscope (Digital Instruments) using microfabricated silicon nitride cantilevers with a force constant of 0.38 N/m.

Results and Discussion

Al(Poly) Foil. The AES spectra of an aluminum foil prepared by the methods described in the previous section (see Figure 1) displayed prominent peaks in the region 50–100 eV characteristic of the clean metal, including its major LMM Auger transition at 68 eV and plasmon losses at 52 eV.²³ Except for the peaks at 200 and 215 eV, attributed to Ar embedded into the lattice during sputtering, no other features could be discerned up to the highest energies examined. Particularly noticeable is the absence of the oxygen peak at ca. 505 eV, which could not be detected by AES even at a much higher sensitivity (see Figure 1), setting an upper limit for this impurity of less than ca. 0.01 monolayer (ML) equiv.

The first cyclic voltammogram of a clean Al foil in PEO(LiClO₄) at 333 K, shown in dotted lines in Figure 2, was

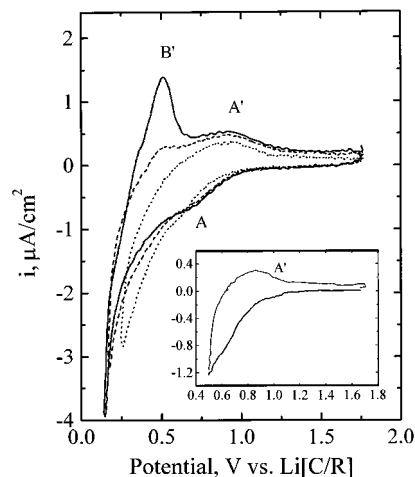


Figure 2. First (dotted line), second (dashed line), and third (solid line) cyclic voltammograms recorded in sequence for a clean Al foil reversed at increasingly more negative potentials, i.e., $E_{\text{rev}} = 0.25, 0.15$, and 0.1 V vs Li[C/R]. This series was initiated at the measured open-circuit potential, i.e., 1.75 V.

initiated at the open-circuit potential (OCV = 1.75 V vs Li[C/R]), a value which is about 0.7 V lower than that observed by Dey²⁴ for slightly oxidized aluminum surfaces. As indicated in the figure, the current during the first linear scan in the negative direction was negligible down to about 1.0 V. This behavior is not necessarily indicative of cleanliness, as impurities present in the PEO(LiClO₄) solution, e.g., oxygen and water, would be expected to react with Al upon assembling the cell (without contributing to the external current) to yield highly irreducible species, e.g., Al oxides and/or oxyhydroxides. However, based on the pre-electrolysis time and the thickness of the molten film, and assuming reasonable values for the diffusion coefficients of species in PEO, it may be concluded (as the experiments seem to indicate) that the amount of reducible impurities in the film following this procedure would, indeed, be negligible and certainly far below that required to form a monolayer on the Al surface.

The increase in the current observed at potentials more negative than 1 V may be ascribed to UPD of Li into Al (see below) and to the onset of Li diffusion into Al to form the corresponding alloy. Reversal of the scan at a potential E_{rev} of ca. 0.25 V yielded a small and rather broad stripping peak (A') centered at ca. 0.8 – 0.9 V, followed by a region in which the current was positive and constant. The second scan in the negative direction revealed a clearly identifiable shoulder centered at ca. 0.7 V (A) and, following reversal at $E_{\text{rev}} = 0.2$ V, a new feature, B', and a much better resolved peak A'. In the subsequent scan, for which E_{rev} was slightly more negative, the magnitude of B' increased markedly, whereas that of A' remained unaffected. Also noticeable as E_{rev} was decreased was the increase in the (constant) current during the scan in the positive direction for potentials higher than 1.25 V. The complementarity of peaks A and A' was demonstrated in an independent experiment in which the potential scan was restricted between 0.5 and 1.3 V (see the inset of Figure 2), lending credence to the view that these features are derived from the UPD of Li on Al.

Experiments in which E_{rev} was only slightly larger than 0.0 V yielded very large B' peaks (see, for example, Figure 3), as would be expected for the formation of one of several bulk Li/Al alloys (see below). It is on the basis of this behavior that Al has been considered as an alternate Li storage electrode for battery applications without the problems associated with

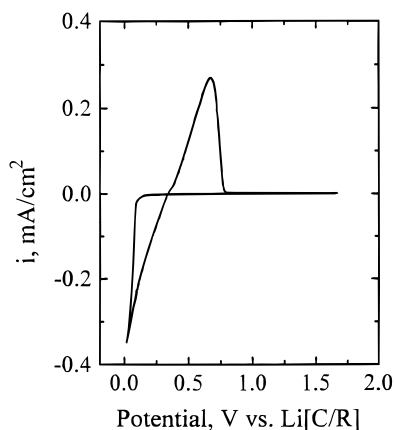


Figure 3. Cyclic voltammogram for a clean Al foil in the range 0–1.75 V vs Li[C/R]. The prominent peak in the scan in the positive direction is attributed to the stripping of Li from the LiAl alloy lattice.

dendrite formation found for pure Li electrodes.¹⁵ Further insight into this phenomenon was gained from measurements involving Li deposition on Al films vapor deposited on BDD, to be described in the following section.

The position of peak A' in Figure 2, i.e., 0.9 V, is consistent with Kolb–Gerischer's UPD correlation,^{2c} which predicts a UPD shift corresponding to half the difference between the work functions Φ of the substrate (sub) and adsorbate (ads) in their bulk forms, i.e., $\Delta U_p = \frac{1}{2}(\Phi_{\text{sub}} - \Phi_{\text{ads}})$. According to values reported in the literature,^{25,26} i.e., $\Phi_{\text{Al}} = 4.2$ eV and $\Phi_{\text{Li}} = 2.25$ eV, ΔU_p would be ca. 0.98 eV, which is also in good agreement with calculations based on density functional theory and the jellium model reported by Lehnert and Schmickler^{7,8} for the adsorption of sp group elements at submonolayer coverages on the low-index faces of Al. For the case of Li, the theoretical UPD shifts on Al(111) (with honeycomb structure), Al(100), and Al(110) were found to be 0.15, 0.64, and 1.78, respectively. On this basis, the Al surface used in this work appears to be composed of a distribution of single crystalline patches, as would be expected for a polycrystalline substrate.

Aluminum Films Supported on Boron-Doped Diamond Substrates. As was mentioned in the Introduction, BDD offers unique advantages for studies of the electrochemical properties of thin films, as it exhibits a featureless and very low capacitive background.^{19,20} In addition, BDD displays no affinity for traditional adsorbates, such as halides and UPD metals, nor does it form electrochemically deposited alloys with any known materials, including Li.¹⁹ Advantage was taken of these unique characteristics to examine Li deposition on sufficiently thin Al films to form Li/Al alloys over relatively short periods of time under conditions in which Al becomes the limiting reagent. Insight into the composition of alloys thus formed could, in principle, be gained by coulometric analysis of linear scans in the positive direction so as to strip Li from the host lattice.

Figure 4 shows AES in the region 0–550 eV of three Al layers of different thickness, τ_{Al} , vapor deposited on BDD films on substrates grown in our laboratories (b and c) or obtained from a commercial source (d), acquired just prior to the electrochemical experiments. Specimen c was obtained by evaporating Al onto the Al/BDD/Si specimen b, after its electrochemical properties had been examined. Based on the time of deposition, τ_{Al} for these specimens increased in the sequence $b < c < d$, as further evidenced by a corresponding decrease in the relative peak-to-peak intensity of the C AES feature at 272 eV. For comparison, the AES spectrum of the bare BDD/Si substrate produced in this laboratory is shown in

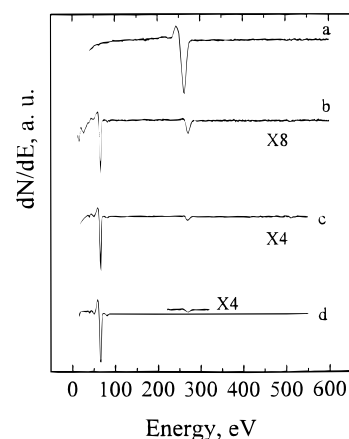


Figure 4. Auger electron spectra for a clean boron-doped diamond film supported on silicon (BDD/Si, curve a) and for Al films vapor deposited on BDD/Si for different lengths of time (curves b–d). The relative peak-to-peak heights of the carbon and aluminum features at 251 and 75 eV, respectively, provide a qualitative measure of Al film thickness (see Table 1).

TABLE 1: Composition and Estimated Thickness of Al Films Vapor Deposited on Boron-Doped Diamond Films Supported on Si

sample	composition (%)	thickness (nm)	stripping charge ^a (mC/cm ²)
b	C (24.35), Al (75.65)	1.1	1.13
c	C (8.5), Al (91.5)	1.9	15.75
d	C (2.0), Al (98.0)	4.2	83.57

^a These values were obtained from a linear scan at 5 mV/s obtained after holding the potential at either 0.0 V for 10 min (b) or 0.025 V vs Li[C/R] for 5 min (c and d).

curve a in this figure. It must be stressed that the very small amount of carbon found in the thickest specimens may be ascribed to a carbon impurity in the film and not necessarily to the underlying BDD. Based on AFM and high-resolution SEM images recorded in this and other laboratories,²⁰ BDD films grown via the hot filament chemical vapor deposition (HFCVD) technique consist of small crystallites, about 1–10 μm in size, with surface roughness of about 1 μm . Furthermore, AFM images obtained in air from a section of sample c (Table 1), away from the area where the electrochemical experiments were performed, recorded after such measurements were completed (see Figure 5), indicated that the oriented BDD crystallites are covered with a highly corrugated overlayer attributed to aluminum oxide with an overall rms roughness of ca. 12 nm and, thus, much higher than that of the underlying substrate. On this basis, estimates of the amount of Al (and, therefore, τ_{Al}) based on the homogeneous attenuation model²⁷ may be subject to large uncertainties. Nevertheless, calculations based on this model, using elemental AES sensitivity factors reported in the literature,²⁸ yielded τ_{Al} values of 1.1, 1.9, and 4.2 nm for the Al/BDD/Si specimens b, c and d in Figure 4, respectively (see Table 1).

A series of cyclic voltammograms for different E_{rev} values obtained with the thinnest Al film on BDD/Si ($\tau_{\text{Al}} = 1.1$ nm) in PEO(LiClO₄) at 333 K are shown in Figure 6. The first of these scans (dotted line) was initiated close to the measured open-circuit potential, i.e., 1.1 V. In direct analogy with the behavior found with the Al foil, as E_{rev} decreases, the height of the peak attributed to the stripping of Li from the Li/Al alloy(s) increases, making the UPD stripping peak centered at 0.8–0.9 V less noticeable.

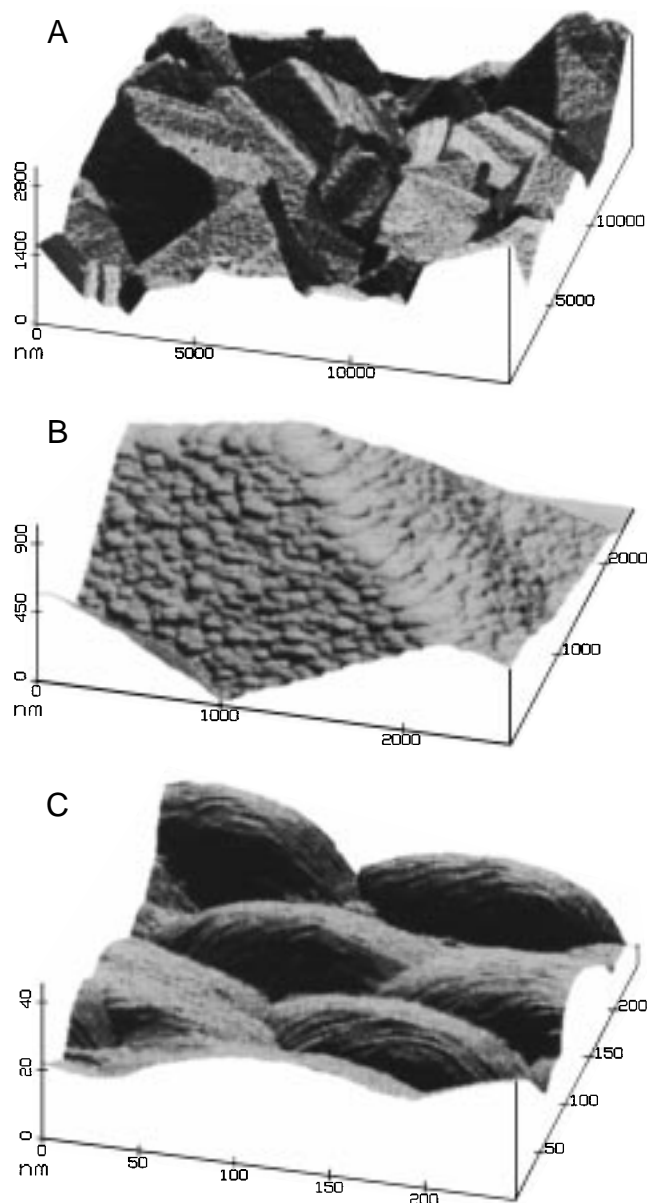


Figure 5. AFM image of a section of sample c (Table 1) not exposed to the PEO(LiClO₄) film obtained in air after the electrochemical experiments were completed (see text for details) at three different magnifications (A, 15 × 15 μm; B, 2.5 × 2.5 μm; C, 0.25 × 0.25 μm).

Polarization of this specimen at a potential of 0.0 V for 10 min yielded a much larger stripping feature (see dotted line in panel b, Figure 7) and a shift in the position of the peak maximum toward more positive potentials, followed by a region of rather constant current of the same magnitude as that observed for the voltammogram with $E_{\text{rev}} = 0.025$ V. Similar experiments involving two thicker Al/BDD/Si films (see panels c and d in that same figure) yielded qualitatively the same results; i.e., after the potential was held at 0.025 V for 5 min, the charge under the peak was larger than that observed in the cyclic voltammetry reversed at the same potential for each of the specimens. Table 1 shows values of the charge under the entire scan in the positive direction, Q_+ , determined from the scanning and holding experiments for the Al/BDD/Si films as a function of their thickness using the zero current axis as a baseline. Based on these data, it is evident that Q_+ , which may be regarded as a measure of the amount of Li in the Al lattice, increases with the Al film thickness. Unfortunately, uncertainties in the actual

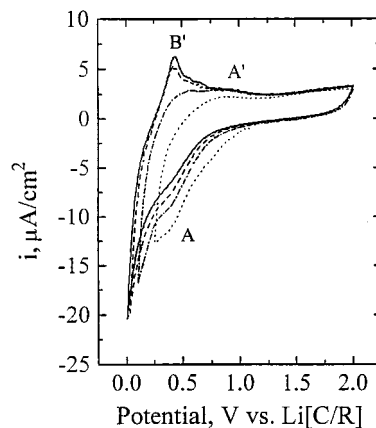


Figure 6. First (dotted line), second (dash-dot line), third (dash line), and fourth (solid line) voltammograms recorded for the thinnest Al film on BDD/Si at increasingly more negative reversal potentials.

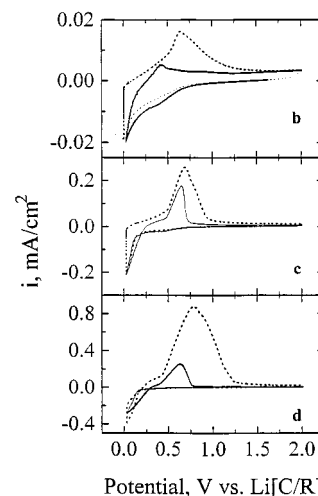


Figure 7. Cyclic voltammograms for the three Al films supported in BDD/Si described in Figure 4 in (LiClO₄)/PEO solutions at 55 °C (solid line). The curves in dotted lines were obtained by holding the potential at 0.0 V for 10 min (upper panel) and 5 min (two lower panels) after a linear scan from 2.0 V and then continuing the scan in the positive direction at the same original scan rate.

amounts of Al in the films due to the dubious assumptions of the homogeneous attenuation model as applied to this system preclude a more quantitative analysis of these data, making it impossible to draw definite conclusions regarding the stoichiometry of the alloy. For example, the Li/Al ratio for some of the specimens, based on AES and electrochemical data, exceeds the saturation value expected from the Li/Al phase diagram at the temperature at which these experiments were carried out. More specifically, the maximum amount of Li in Al at room temperature cannot exceed values larger than 68 (atomic %); i.e., any additional lithium would be present as pure metal in equilibrium with the alloy. These difficulties could be circumvented by installing a quartz crystal microbalance in the chamber that will enable measurements of Al deposition rates, and hence accurate determination of the absolute amount of Al in the films.

Conclusions

The electrochemical properties of clean aluminum in LiClO₄-(PEO) solutions have been investigated in ultrahigh vacuum at temperatures of about 55 °C using a foil and films of various thicknesses deposited on boron-doped diamond supported on Si substrates. The results obtained revealed a rather clearly defined peak in the scan in the positive direction centered at

ca. 0.90 V, attributed to the stripping of UPD Li on Al. This potential is consistent with that predicted from Kolb–Gerischer’s correlation and also with the theoretical calculations by Schmickler et al. for Li adsorption on a distribution of low-index Al single-crystal facets. Polarization of Al at potentials slightly positive to Li bulk deposition for several minutes gave rise to a prominent peak centered at about 0.6 V, ascribed to the stripping of Li from one or more LiAl alloys. The amount of stored Li was found to increase with the thickness of the Al film; however, uncertainties in the actual amount of Al did not allow more quantitative conclusions to be drawn.

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