

Electrochemistry of AlCl₃-based Melts in UHV

Matt Johnston[†], Jae-Joon Lee[‡], Kraig Wheeler[‡], Gary S. Chottiner^o, Barry Miller[†] and Daniel Scherson[†].
Departments of Chemistry[†] and Physics^o, Case Western Reserve University, Cleveland OH 44106.
Department of Chemistry[‡], Delaware State University, Dover, DE 19901.

The application of room temperature molten salts to Ultra High Vacuum electrochemical investigations continues our interest in such UHV techniques for electrochemical science. Room temperature molten salts have singular properties of technological importance¹⁻³ as well as intrinsic interest. The two most interesting features from the UHV standpoint would be the wide temperature range and low vapor pressure³. Of high priority is the is the electrodeposition of Al and Al-based alloys from AlCl₃/1-ethyl-3-methylimidazolium chloride (EMIC) melts of appropriate Lewis acidity.^{4,5}

We have earlier studied fundamental aspects of both bulk and underpotential deposition of aluminum onto many substrates, including tungsten, gold and boron doped diamond, of ongoing interest to our group. Although diamond has a weak affinity for adsorption of species, other surfaces do interact and films are formed by exposure to oxygen or organic impurities. The following is part of our continuing research effort to incorporate surface analytical techniques in the preparation and characterization of electrode materials in acidic AlCl₃/EMIC melts in UHV environments to avoid the problems arising from the presence of surface contaminants, which can affect the interfacial properties of electrodes and the data interpretation.

All electrochemical measurements were preformed in a UHV chamber equipped with a single pass cylindrical mirror electron energy analyzer for Auger electron spectroscopy (AES), an Ar⁺ ion sputtering gun for the cleaning of metal surfaces and a mass spectrometer for residual gas analysis. A gold rod about one inch long and 0.25 inch in diameter was used as the working electrode. The electrode was cleaned by a series of Ar⁺ ion sputterings followed by thermal annealings. The surface composition was determined by AES. An acidic melt sample was prepped in a nitrogen filled glove box system (VAC), equipped with moisture and oxygen analyzers, using previously described methods,⁷ and transferred to a UHV compatible glass/metal valved flask. The sealed flask was then attached to the one of the ports on the electrochemical arm. The room temperature molten salt was thoroughly degassed over a number of days and turned upside down above the cell chamber for transfer. The valve was then opened carefully and a few ml of liquid was transferred to the cell. The cell was of an all Teflon construction incorporating an Al wire that served as the counter and reference electrode. The cell was attached to a magnetically coupled manipulator for transferal to the main experimental chamber. The pressure in the chamber prior to transfer is 2x10⁻¹⁰ torr. The gate valve connecting the electrochemical arm and the main experimental chamber was opened and the cell transferred. The cell is completed by forming a hanging meniscus between the suspended gold electrode and the melt. Once this arrangement was completed the electrochemical experiments were initiated.

Figure 1. shows a number of cyclic voltammety plots of the precleaned and characterized gold electrode. Most of the features observed have been reported by other

workers and are typical of the alloying behavior found for the Al/Au system. The pressure at the end of the experiment which lasted for eight hours was in the 5x10⁻⁹ torr range.

The decision to use gold in these experiments was made in order to form comparisons with experimental data of glovebox experiments. The passive nature of the gold surface to atmospheric oxygen make the result easier to interpret than those previously obtained for a more reactive tungsten surface which had its native oxide layer removed⁸. Without the low vapor pressure of the ionic liquids used these experiments would be beyond the reach of UHV electrochemists. The desire to understand the interfacial electrochemistry of UHV pretreated versus conventionally treated electrodes at atmosphere has always been an intriguing thought experiment, but now we show that it is possible, although demanding, to study the behavior of metals prepared and characterized in UHV, including metal UPD and bulk deposition, and fundamental aspects of the structure and properties of well defined single crystal metal-ionic liquid interfaces.

Acknowledgements.

This work was supported in part by the US Department of Energy, Office Of Basic Energy Sciences, and also by a grant from NEDO, Japan..

References

1. C.L.Hussey, *Pure & Appl. Chem.*, **60**, 1763 (1988).
2. J.S. Wilkes, J.A.Levisky, R.A. Wilson and C.L. Hussey, *Inorg. Chem.*, **21**, 1263 (1982).
3. C.L. Hussey, in *Chemistry of Nonaqueous Solutions: Current Progress*, G. Mamantov and A.I. Popovs, p. 225 New York, NY (1994).
4. J. Robinson and R.A. Osteryoung, *J. Electrochem. Soc.*, **127**,122 (1980).
5. T.J. Melton, J. Joyce, J. T. Maloy, J. A. Boon and J. S. Wilkes, *J. Electrochem. Soc.*, **137**, 3865 (1990).
6. P.K. Lai and M. Skyllas-Kazacos, *Electrochim. Acta.*, **32**, 1443 (1987).
7. J-J. Lee, I. Bae, D.A. Scherson, B. Miller and K. Wheeler, *J. Electrochem. Soc.*, **147**, 562 (2000).
8. M. Johnston, J-J. Lee, K.A. Wheeler, G.S. Chottiner, B. Miller, D.A. Scherson *Abstract No. 641*.Toronto meeting, Spr. 2000.

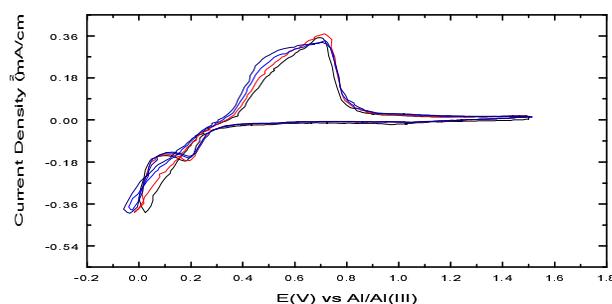


Fig. 1. Series of cyclic voltammograms for a clean and characterized Au electrode in acidic (N=1.1) AlCl₃/EMIC melts recorded in UHV (~6 x 10⁻¹⁰ torr). Scan rate=20 mV/s.