Galvanostatic Pulse Plating of Al Metal in Room-Temperature Chloroaluminate Ionic Liquids

Li-Hsien Chou and C.L. Hussey

Department of Chemistry and Biochemistry, University of Mississippi, MS 38677, USA

Aluminum is a widely used material for corrosion resistant coatings. From a thermodynamic perspective, it is a very active metal. However, its excellent corrosion resistance stems from the formation of a robust, self-healing ~50 nm thick barrier oxide film, which is formed spontaneously upon exposure to air at ambient temperature. However, aluminum cannot be plated from aqueous solutions because hydrogen is evolved before most Al(III) species are reduced to Al. A number of commercial Al plating processes have been developed. Typically, these processes are based on pyrophoric mixtures of $AlCl_3$ or $AlBr_3$ with $LiAlH_4$ dissolved in suitable organic solvents, such as ethers or mixtures of substituted benzenes.

The first report in which a room-temperature haloaluminate ionic liquid was used to plate Al appeared in 1948.[1] Such ionic liquids, particularly those based on mixtures of $AlCl_3$ and quaternary ammonium chloride salts, have many safety and convenience advantages over the currently used commercial Al plating baths. In this work, we report the pulsed current plating of Al on Cu, steel, and stainless steel substrates from the Lewis acidic $AlCl_3$-1-ethyl-3-methylimidazolium chloride (EtMeImCl) ionic liquid containing organic co-solvents. Compared to DC methods, pulsed current techniques often lead to electrodeposited metals with smaller grain size and greater brightness, as well as less internal stress and correspondingly superior corrosion resistance.

Some preliminary results for Al films electrodeposited on copper are shown in Figures 1-3. The corrosion resistance of these films was interrogated with electrochemical impedance spectroscopy (EIS), open circuit potential (OCP) measurements, and potentiodynamic polarization techniques in aqueous NaCl. Complex plane impedance plots (Fig. 1) revealed a single time constant in the frequency range that was investigated. Fitting of the Randles-Ershler equivalent circuit model gave a polarization resistance (R_p) that was one order of magnitude larger for the Al film prepared with the pulsed current method. OCP experiments are shown in Figure 2, and they indicate that the Al film prepared with pulsed current is more positive (noble) than that resulting from DC plating. Potentiodynamic polarization plots (Fig. 3) show the typical results expected for Al, i.e., both DC and pulsed current films display a stable passive region characterized by a very small potential-independent current with a rise in current as the pitting potential is reached at more positive potentials. However, the pitting potential for the film prepared by pulsed current plating is more positive than that for the DC film. The results of this investigation with respect to the surface structure, grain size, and brightness, will also be discussed.

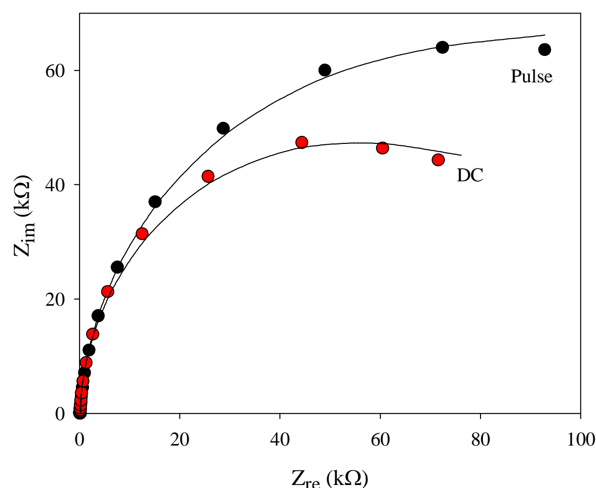

Figure 1. Complex plane impedance plots of Al films in 0.1 M NaCl. Solid line is the Randles-Ershler model.

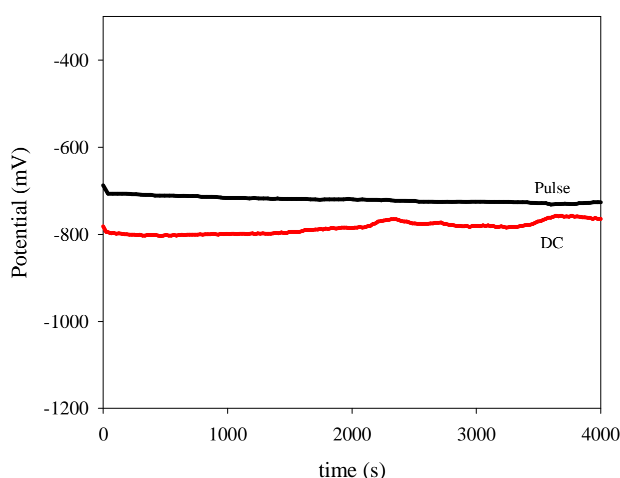

Figure 2. OCPs of the Al films as a function of time in 0.1 M NaCl.

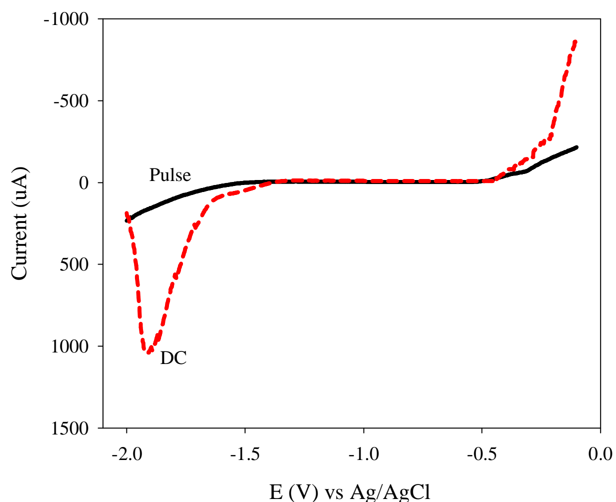

Figure 3. Potentiodynamic polarization plots of the Al films in 0.1 M NaCl.

ACKNOWLEDGEMENT

This work was funded by the Strategic Environmental research and Development Program (SERDP) through contract DE-AC05-00OR22725 to Oak Ridge National Laboratory.

[1]F. H. Hurley, U.S. Pat. 2,446,331 (1948).