Potential oscillation was observed during the template-free galvanostatic deposition in the 58/42 mol% AlCl3/trimethylamine hydrochloride ionic liquid, and resulted in the formation of unique periodic (accordion-like) aluminum wires with variable periodicity and diameter controlled by the deposition current density. Factors leading to this phenomenon are postulated. © The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial No Derivatives 4.0 License (CC BY-NC-ND, http://creativecommons.org/licenses/by-nc-nd/4.0/), which permits non-commercial reuse, distribution, and reproduction in any medium, provided the original work is not changed in any way and is properly cited. For permission for commercial reuse, please email: oa@electrochem.org. [DOI: 10.1149/2.0021507eel] All rights reserved.

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Experimental

All the electrochemical experiments were carried out in the quasi-enous AlCl3/TMHC (58/42 mol%) in a N2-filled glove box at 38 °C using a conventional three-electrode cell. An Al spiral wire (Alfa Aesar, 99.95%) immersed in the bulk IL was used as the counter electrode, the reference electrode was an Al wire in a fritted glass tube filled with the same IL. The working electrode was a W wire (diameter =0.5 mm). The electrochemical experiments were performed with an EG&G PARC Model 263A potentiostat/galvanostat controlled with EG&G Model 270 software. High-resolution scanning electron microscopy (HITACHI, SU8000) was used to examine the morphology of the deposits.

Results and Discussion

Potential oscillation during galvanostatic electrodeposition and current oscillation during potentiostatic electrodeposition are of interesting because these phenomena often associated with the production of deposits having interesting spatial patterns in the micro- or nano-scale. Many examples acquired in aqueous systems have been reported including tin metal latticework consist of cuboids connected by needles, stacked alternated layers of metals or alloys dendrites, and metal wires with periodically changed diameters. Often, the oscillation is associated with negative differential resistance (NDR), and has been attributed to the reactions such as formation of passivation layer, autocaltotic growth, adsorption of additives (levelers and accelerants), and restricted mass transport of ionic.

Ionic liquids (ILs) have attracted numerous interests in electrochemistry and electrodeposition especially for the deposition of materials such as Al that are difficult to obtain from aqueous baths. Materials with various morphologies, specifically, metals/ alloys wires, have been electrodeposited from ILs with and without the need of template. Nevertheless, reports on electrochemical oscillation in IL are very limited. Schaltin et al. discussed the current oscillation during potentiostatic electrolysis of EMIC IL, containing both Cu(II)/Cu(I), and found the presence of both Cu(II) and Cu(I) is essential for the oscillation to occur. Here, we report the potential oscillation during the template-free galvanostatic deposition of Al from a quasi-enous 58/42 mol% AlCl3/trimethylamine hydrochloride (AlCl3/TMHC) IL, which leads to the formation of Al wires with diameters change periodically. According to the literature, the complex ion chemistry in the AlCl3/TMHC is similar to that for the AlCl3/1-ethyl-3-methylimidazolium chloride (AlCl3/EMIC) ILs, but the former ILs exhibit higher melt points and higher viscosities than the later ILs do. To our knowledge, galvanostatic deposition of Al from the AlCl3/EMIC ILs has been studied, but potential oscillation has not been reported.

Referring to previous work, the reducible Al(III) species in this IL is Al2Cl7−, and the bulk electrodeposition of Al proceeds according to the overall equation:

$$4\text{Al}_2\text{Cl}_7^- + 3\text{e}^- \rightarrow \text{Al} + 7\text{AlCl}_4^- \quad [1]$$

The working electrode potential is a function of the concentrations (activity) of Al2Cl7− and AlCl4−. It is expected that the potential shifts negatively as the reduction proceeds because of the generation of AlCl4− and consuming of Al2Cl7−. The potential of the working electrode recorded as a function of the time during the electrolysis at a current density of 0.25 mA/cm2 is shown in Fig. 1A. This figure shows that the potential oscillates between two extreme potentials (Eo and Ei). After the deposition, the deposited sample was carefully washed with anhydrous ethanol, and dried for further characterization. Fig. 1B shows the SEM images of the Al deposits. It can be seen that the W substrate is covered by Al nanowires that display a unique segmented morphology; that is, the nanowires periodically change their diameters along the growth direction.

The potential oscillation was further studied at various current densities: 0.25 to 1.25 mA/cm2. The E-t curves recorded for these experiments are presented in Fig. 1C. This figure shows that during the electrolysis, the potential oscillates between a base potential, Eo, and a more negative peak potential, Ep. While the Eo remains at a relatively constant value throughout the electrolysis, the Ep varies from time to time. In general, a strong oscillation is followed by several weak oscillations. Furthermore, increasing the current density shifts Eo negatively. Collected in Figure 1D are the periods of the potential oscillation measured at various current densities as a function of electrolysis charge density, Q, which is the product of the current density, j, and the electrolysis time, t, that is Q = j × t. As can be seen, the oscillation period decreases with increasing current density and decreasing electrolysis charge. The SEM images of the Al deposits samples shown in Fig. 2 shows that while the periodic (accordion-like) structure of the Al wires is clearly seen in the sample obtained at 0.25 mA/cm2, such periodicity become less obvious and the Al wire diameter decreases as the current density increases. This behavior is in accordance with the decrease in the potential oscillation period.

The mechanism for the potential oscillation and formation of periodic Al wires is complicate and not known at present time, and we can only propose some possible factors related to it. Referring to Fig. 2 and the literature, the potential oscillation is divided into 4 stages. At stage 1, a polygonal deposit forms and grows 3-dimensionally. As the deposition going, the Al2Cl7− concentration quickly depletes with the generation of AlCl4− at the electrode/solution interface, making the IL within this region less acidic and more viscous and resistant. Therefore, the potential shifts negatively. The continuous deposition relies on the supply of Al2Cl7− through diffusion onto the growing site accompanied with diffusion layer thickening and resistance increase. At stage 2, the diffusion layer thickening and the increased...
solution resistance has reached a state that the deposition toward most directions are slowed down, and the Al deposit has to grow toward the crystal peak point front where the effective current density is highest. As a result, the diameter grows at this point becomes narrow. The viscosity decreases and the resistance decreases as the Al wire tip grows into the front solution which contains higher $\text{Al}_2\text{Cl}_7^{-}$ concentration, leading to positive potential shift until it reaches stage 3. At stage 3, the $\text{Al}_2\text{Cl}_7^{-}$ concentration surrounding the growing Al wire is high enough and the resistance is low enough to support the lateral expanding of the Al wires, consequently the diameter gets wider. As the deposition continuous, the $\text{Al}_2\text{Cl}_7^{-}$ concentration depletes and the potential shifts negatively again until it reaches stage 4 where the growth of the deposit toward the front tip resumes. By repeating these stages, periodic Al wires are formed. Potential oscillation disappeared when the viscosity of the IL is reduced by increasing the temperature above 50°C and/or the mass transport is enhanced by introducing mechanic stirring. In addition, the adsorption and desorption of the IL cations during the positive and negative, respectively, potential shift may also contribute to the variation of resistance and growth rate at the growing parts. It is known that TMHC is used as additive for electrodeposition studies.27

In summary, periodic Al wires are electrodeposited from a quiescent $\text{AlCl}_3$/TMHC IL. The growth of periodic structure is associated with the potential oscillation, which may relate with the diffusion layer thickening and electrolyte resistance variation during the deposition. The periodicity and wire diameter vary with the deposition current density. Electrodeposition of other metals with periodic structures in other ILs will be studied in order to gain more understandings of this process.
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References


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