Electrodeposition and Electrodissolution of Aluminum in Ionic Liquid Electrolytes

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Aluminum (Al) is an attractive anode material for energy storage and conversion. Its relatively low atomic weight of 26.98 along with its trivalence give a gram-equivalent weight of 8.99 and a corresponding electrochemical equivalent of 2.98 Ah/g, compared with 3.86 for lithium, 2.20 for magnesium and 0.82 for zinc. Additionally, aluminum is both an abundant (8.1% in Earth's crust) and relatively inexpensive metal (2~3 USD/kg) [1]. However, aluminum is so much less noble than hydrogen, so it probably cannot be deposited from aqueous solution [2]. Therefore, aqueous Al-based battery is considered as primary battery which cannot easily be recharged after one use and is discarded following discharge, whereas it may work fine as secondary battery in ionic liquid system. It has been published that the deposition (charge) and dissolution (discharge) of aluminum in chloroaluminate ionic liquid consists of aluminum chloride ($AlCl_3$) and 1-ethyl-3-methylimidazolium chloride (EMIC) worked properly [3]. When the molar ratio of $AlCl_3$/EMIC is larger than 1, the ionic liquid shows Lewis acidity. In acidic chloroaluminate ionic liquid, $Al_2Cl_7^-$ is a predominant species and aluminum deposition/dissolution can proceed with the reduction of $Al_2Cl_7^-$ [4], as follows:

$$4Al_2Cl_7^- + 3e^- \rightleftarrows Al + 7AlCl_4^- \qquad (1)$$

Kishimoto *et al.* [5] studied cyclic voltammograms on Au electrodes in 2:1 molar ratio $AlCl_3$-EMIC ionic liquid at various temperatures (scan rate: 20 mVs^{-1}). The CV results indicated that the anodic and cathodic peak current increased with increase of temperature [5]. However, a relatively low coulombic efficiency (~70 % at 25 ^oC) of Al in the ionic liquid was reported [5]. Moreover, little is known about the stability of $AlCl_3$-EMIC ionic liquid under cyclic deposition/dissolution of Al.

In this work, the authors studied the deposition and dissolution behavior of aluminum on carbon glass electrode in an acidic chloroaluminate ionic liquid at a constant high scan rate. Experimentally, 2000 cycles of Al deposition/dissolution was achieved at a scan rate of 500 mVs^{-1}, and a high coulombic efficiency (~93%) was obtained.

Ionic liquids were prepared under a high purified argon atmosphere (H_2O and O_2 < 5 ppm) in a glove box (Innovative Technology, PL2GB). EMIC-$AlCl_3$ ionic liquid (2:3 molar ratio) was prepared by slow addition of anhydrous $AlCl_3$ (>99.0%, Alfa Aesar) to EMIC (97%, Acros) using a magnetic stirrer. Electrochemical experiments were carried out by using a three-electrode electrochemical cell. The working electrode was a carbon glass. Counter and reference electrodes were aluminum wires (99.999 wt.%, Alfa Aesar). Cyclic voltammetry measurement was performed with a potentiostat/galvanostat (AutoLab, PGSTAT302N).

Fig. 1 plots the coulombic efficiency of Al deposition (charge) and dissolution (discharge) *vs*. cycle number on carbon glass electrode in EMIC-$AlCl_3$ (2:3 molar ratio). The coulombic efficiency was calculated from cyclic voltammetry measurements. In summary, the coulombic efficiency was kept larger than 93% up to 2000 cycles. The high scan rate (500 mVs^{-1}) implies that the EMIC-$AlCl_3$ ionic liquid can be applied as the electrolyte for rechargeable Al-based batteries requiring high charge/discharge rate.

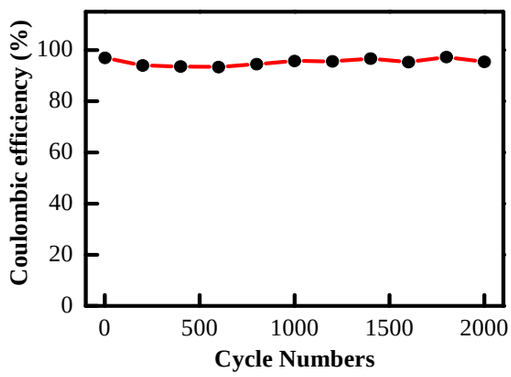

Fig. 1. Plot of coulombic efficiency *vs*. cycle number for Al deposition and dissolution on carbon glass electrode in EMIC-$AlCl_3$ (2:3 molar ratio) up to 2000 cycles between -0.5 and 2 V (*vs*. Al) at a scan rate of 500 mV/s^{-1}.

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