



# Anodic behavior of Mg in acidic AlCl<sub>3</sub>–1-ethyl-3-methyl-imidazolium chloride ionic liquid



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## ABSTRACT

In this paper, anodic behavior of Mg in acidic AlCl<sub>3</sub>–1-ethyl-3-methyl-imidazolium chloride (AlCl<sub>3</sub>–EMIC) ionic liquid was investigated by conducting linear sweep voltammetry, chronoamperometry and chronopotentiometry. The viscosity of Mg dissolved ionic liquid and the surface morphologies of Mg were characterized using an Ostwald viscometer and a scanning electron microscopy, respectively. The results showed that the oxide film on the surface of Mg had great effects on the anodic behavior. The dissolution of Mg under anodic polarization occurred after the breakdown of oxide film. A viscous layer was observed forming at the interface of Mg/ionic liquid during the dissolution process. The formation of viscous layer was attributed to the accumulation of Mg dissolved AlCl<sub>3</sub>–EMIC ionic liquid at the interface, which was of high viscosity. With a viscous layer formed in the anodic process, the etched surface of Mg anode was homogeneous and flat without any etching pits. Otherwise, the Mg showed a morphology of pitting on the surface.

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## 1. Introduction

Ionic liquids, also called room temperature molten salts, are composed of entirely ions, having melting temperature below 100 °C. The attractive properties of ionic liquids, like intrinsic ionic conductivity, wide electrochemical potential windows, good thermal stability, non-volatility and non-flammability, make them be “the third solvent” besides water and organic solvents [1,2].

The development of ionic liquids in recent decades opens new frontiers in the researches on the surface engineering of materials [3]. Ionic liquids are promising electrolyte for many electrochemical processes of metals, like electropolishing [4,5], electrochemical micromachining [6], electrolytic etching [7,8], extraction and refining of metals [9–11], etc. For all these applications, fundamental studies on the anodic behavior of metals in ionic liquids are highly demanded. These studies can also provide guidelines for the researches on corrosion behaviors of metals in ionic liquids and for the choice of materials for insoluble anodes in electrodeposition.

The anodic behavior of metals has been intensively studied in aqueous solutions. However, reports on the anodic behaviors in ionic liquids are still limited. Wang et al. [12] investigated the corrosion behaviors of various metals in dicyanamide (DCA) based ionic liquids, which showed that Ni, Ti, Al and 304 stainless steel

exhibit well resistance against anodic dissolution, while Cu, Mg and carbon steel show severe dissolution under anodic polarization. Chen et al. [13] reported that Ti could be passive in choline chloride (ChCl) based ionic liquids, while Abbott and his colleagues' studies [4] showed that many stainless steels (SS410, 302, 304, 316 or 347) will dissolve in these ionic liquids. In bis (trifluoromethylsulfonyl) amide (Tf<sub>2</sub>N) based ionic liquids, Fe and Al could not be significantly dissolved or corroded, but Cu and Ni exhibit active dissolution behavior [5,6,14,15]. The studies on anodic behavior of metals in ionic liquids so far suggest that it strongly depends on the metal electrodes and ionic liquids employed.

AlCl<sub>3</sub>–1-ethyl-3-methylimidazolium chloride (AlCl<sub>3</sub>–EMIC) ionic liquid is a kind of water-free electrolyte, which is a promising medium for the electrodeposition of Al coating and its alloy coatings on water-sensitive materials like Mg alloys, NdFeB and rare earth metals to improve their corrosion resistance, as well as on steels to avoid the problems like hydrogen embrittlement caused by electroplating in aqueous solutions [16–19]. For these applications, the key problem is the removal of the natural oxide layer on the substrates, which is a crucial factor to get a strongly adherent coating [19]. Previous studies on the anodic etching behavior of Mg alloys, NdFeB and mild steel in AlCl<sub>3</sub>–EMIC ionic liquid showed that the oxide layers can be completely removed by the electrolytic etching pretreatment [18,20]. However, it strongly depends on whether there is a viscous layer formed at the anode/ionic liquid interface during the etching process [7,20].

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To provide a guideline for the anodic electrolytic etching pretreatment, it is greatly demanded to study the anodic behaviors of metals in  $\text{AlCl}_3$ -EMIC ionic liquid, which are seldom reported. Chang et al. have studied the corrosion behaviors of different materials in  $\text{AlCl}_3$ -EMIC, which shows that Ni and 304 stainless steel exhibit good stability, while Ti, Al, Cu and 316 stainless steel dissolve in this ionic liquid [12,21,22]. In this paper, studies on the anodic behavior of Mg in  $\text{AlCl}_3$ -EMIC ionic liquid were carried out. The mechanism of the anodic behavior of Mg and the formation of viscous layer was discussed.

## 2. Experimental

Anhydrous  $\text{AlCl}_3$  powder (99.99%, Alfa Aesar) was used without further treatment. EMIC was synthesized according to Ref. [23]. The  $\text{AlCl}_3$ -EMIC ionic liquid was prepared by slow addition of  $\text{AlCl}_3$  into EMIC in a beaker at room temperature until the  $\text{AlCl}_3$  to EMIC molar ratio was 2:1. The mixture was continuously stirred by a magnetic bar for one day, and then refined with pure Al wires for one week in order to remove the impurities. The Mg plates (99.95%) used were mechanically polished with SiC papers to a grit of 1200 and then ultrasonically cleaned with acetone in air. The apparent area of the Mg plates for study was  $1 \times 1 \text{ cm}^2$  by sealing the other portion with an adhesive band. The samples were transferred into the glove-box for electrochemical measurements immediately after the mechanical polishing pretreatment except where stated. All the experiments referred to  $\text{AlCl}_3$ -EMIC ionic liquid were performed in an argon-filled glove-box at room temperature, in which the oxygen content and moisture were maintained below 1 ppm.

The electrochemical measurements were conducted on a Princeton Applied Research Parstat 2273 potentiostat/galvanostat using a conventional three-electrode cell. The Mg plate was assembled as the working electrode, while a pure Al plate (99.999%) and a pure Pt wire were used for the counter and reference electrodes, respectively. The linear sweep voltammogram was measured from the open-circuit potential, which was measured by the PAR 2273 potentiostat/galvanostat within a few seconds after the electrochemical measurements started (ca.  $-1.2 \text{ V}$ ), to  $1.0 \text{ V}$  with a sweep rate of  $20 \text{ mV/s}$  at room temperature ( $25^\circ \text{C}$ ). Anodic behavior of Mg in  $\text{AlCl}_3$ -EMIC ionic liquid was studied by chronoamperometry and

chonoamperometry. The potentials for chonoamperometry were  $-1.0 \text{ V}$ ,  $-0.7 \text{ V}$ ,  $-0.3 \text{ V}$ ,  $0.3 \text{ V}$  and  $0.7 \text{ V}$  vs. Pt. The current densities for chonoamperometry were  $2 \text{ mA/cm}^2$ ,  $5 \text{ mA/cm}^2$ ,  $10 \text{ mA/cm}^2$  and  $15 \text{ mA/cm}^2$ .

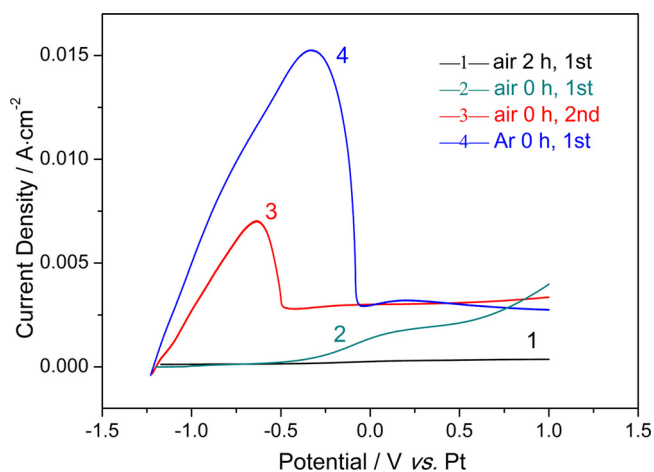
The surface morphologies of the samples were characterized by scanning electron microscope (SEM). The chemical composition of samples was identified by means of an energy dispersive X-ray spectroscopy (EDS) coupled to the SEM instrument. The viscosity of the ionic liquid was measured using an Ostwald viscometer at  $25^\circ \text{C}$ .

## 3. Results

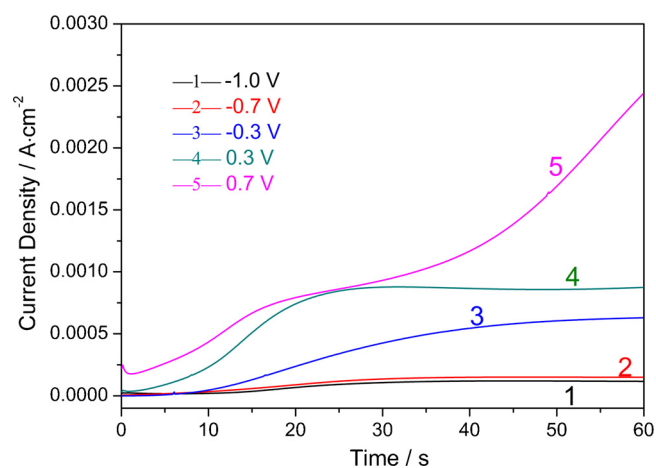
### 3.1. Electrochemical measurements

Fig. 1 demonstrates the linear sweep voltammetry of Mg in  $\text{AlCl}_3$ -EMIC ionic liquid after mechanical polishing pretreatments under different conditions. For the sample with 2 h additional exposure in air after mechanical polishing, the linear sweep voltammetry does not exhibit any features, showing a negligible constant current below  $0.1 \text{ mA/cm}^2$  with the sweep of potential from the starting sweep potential to  $1.0 \text{ V}$  (Curve 1). In contrast, as to the sample assembled for measuring immediately after the polishing in air, it starts to dissolve at the potential ca.  $-0.5 \text{ V}$ . And then the current density increases gradually with the positive shifting of potential. After the first sweep of voltammetry, a second sweep of this sample was deliberately carried out. As shown in Curve 3, dissolution of the sample takes place even at the beginning of second sweep from the starting sweep potential. With the positive shift of potential, the current density increases rapidly up to  $7 \text{ mA/cm}^2$ . However, as the potential increases from  $-0.7$  to  $-0.6 \text{ V}$ , the current density decreases drastically and then keeps constant showing a current plateau at ca.  $3 \text{ mA/cm}^2$ . In addition, the linear sweep voltammetry was also performed for the Mg electrode polished in the glove-box. As shown in Curve 4, the voltammetric response is similar with that observed for the second sweep of the sample polished in air. Dissolution starts from the beginning of sweep, followed by a rapid increasing process to even higher current density up to  $15 \text{ mA/cm}^2$ . Meanwhile, there is also a limiting current plateau observed at ca.  $3 \text{ mA/cm}^2$ .

For a further understanding of the anodic behavior, Mg electrodes were studied under potentiostatic and galvanostatic conditions immediately after polishing in air. Fig. 2 presents the chronoamperometry for the Mg electrode performed at different



**Fig. 1.** Linear sweep voltammetry of the Mg plates in  $\text{AlCl}_3$ -EMIC ionic liquid at  $25^\circ \text{C}$ . (1) first sweep, 2 h additional exposure in air after mechanical polishing pretreatment; (2) first sweep immediately after mechanical polishing pretreatment in air; (3) second sweep after mechanical polishing pretreatment in air; (4) first sweep immediately after mechanical polishing pretreatment in Ar.



**Fig. 2.** Chronoamperometry for the Mg electrode in  $\text{AlCl}_3$ -EMIC ionic liquid at (1)  $-1.0 \text{ V}$ ; (2)  $-0.7 \text{ V}$ ; (3)  $-0.3 \text{ V}$ ; (4)  $0.3 \text{ V}$ ; (5)  $0.7 \text{ V}$  vs. Pt for 60 s.

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