

Electrodeposition of magnesium film from BMIMBF₄ ionic liquid

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Abstract

In this paper, we reported for the first time magnesium electrodeposition and dissolution processes in the ionic liquid of BMIMBF₄ with 1 M Mg(CF₃SO₃)₂ at room temperature. Our study found that complete electrochemical reoxidation of the electrodeposited magnesium film was feasible only on Ag substrate, comparing with the Pt, Ni, and stainless-steel. Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) results showed that magnesium was found in the deposited film and the deposits were dense. The electrodeposition of magnesium on Ag substrate in the ionic liquid was considered to be a reversible process by cyclic voltammetry. Plots of peak current versus the square root of the scan rate were found to be linear, which indicates that the mass-transport process of electroactive species was mainly diffusion controlled. The diffusion coefficient *D* values of electroactive species were calculated from cyclic voltammetry and chronoamperometry, respectively.

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1. Introduction

There are two major interests in developing reversible electrochemical magnesium deposition: Mg deposit for purposes of surface finishing, cathodic protection against corrosion, etc. [1]. The use of magnesium as an anode material for rechargeable nonaqueous batteries [2]. Electrolysis of molten magnesium chloride and thermal reduction of magnesium oxide are the two principal production processes in use today. Although silicothermic reduction has become more important in recent years, most of the magnesium produced today on a worldwide scale is still extracted by molten salt electrolysis [3]. Extensive electrochemical studies of magnesium in molten chlorides have been carried out through the years. There are reports on the behavior of Mg electrodes in high temperature molten salts such as MgCl₂ (725–780 °C) [4], MgCl₂ + NaCl (700–800 °C) [5], CaCl₂ (850 °C) [6], MgCl₂ + MgF₂ (650–700 °C) [7], CaCl₂ + NaCl (550, 727 °C) [8], MgCl₂ + NaCl + KCl [9] and CaCl₂ + NaCl + KCl + MgCl₂ (727 °C) [6]. Some authors found the magnesium reduction reaction in pure molten magnesium

chloride was a quasi-reversible two-step charge-transfer process, preceded by a slow chemical dissociation of polynuclear magnesium complexes [4]. Moreover, in MgCl₂–NaCl system, a three-step electrode process can be handled as a preceding chemical reaction, followed by a two charge-transfer steps with pure charge-transfer process in the high-frequency domain while mixed charge-transfer-diffusion character in the low-frequency region showed by combining ac impedance spectra and galvanostatic relaxation transients [5]. On the other hand, the electrodeposition of magnesium in MgCl₂–MgF₂ and CaCl₂–NaCl was considered to be a quasi-reversible process [7,8]. The effect of the substrate material and impurities in the electrodeposition process were the main subjects of those investigations. A wide variety of substrate materials has been used, but due to industrial applications, iron and stainless-steel are the substrates used by most of the authors, although tungsten, platinum, and glassy carbon have also been used. Some authors also performed nucleation studies during magnesium electrodeposition on foreign substrates. It was found that the magnesium electrodeposition follows an instantaneous nucleation process with three-dimensional growth of the deposit [10].

It is well known, the high liquidus temperature (>100 °C) associated with most inorganic melts precludes their general application, whether practical or fundamental in nature.

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The high temperature associated with inorganic melts frequently places exceptional requirements on either the design of apparatus or the extraneous solutes dissolved in melts, and often adds extraordinary experimental manipulation. Thus, the development of low temperature molten salts for practical or fundamental applications including metal deposition has been an important field of investigation. Room temperature molten salts or ionic liquids are acknowledged as the next generation of electrolytes because of their wide liquid-phase range, low viscosity, lack of volatility, nonflammability, very low vapour pressure and greater thermal and electrochemical stability than aqueous electrolytes and chloroaluminate-type ionic liquids [11,12]. Especially air- and water-stable nonchloroaluminate-type ionic liquids, based on new anions and cations, have gained a great interest in the recent years, in which it is possible to electrodeposit nanoscale light metals and semiconductors [13,14]. The attempts to prepare electrolyte solutions of Mg salts based on room temperature organic molten salts should also be acknowledged [15]. Moreover, investigation has been developed to deposit magnesium from room temperature electrolytes [16,17].

Ionic liquids with BF_4^- generally have low melting point, low viscosity, and high ionic conductivity [11]. In this paper, we report for the first time that magnesium can be electrodeposited in the ionic liquid of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) with 1 M $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ at room temperature. Different substrate materials were tested, although the reported results may be mainly focused on the use of stainless-steel substrate in the ionic liquid.

2. Experimental

2.1. Chemicals

1-*n*-Butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) (Fluka) was dried over molecule sieves in an argon filled glove box (MBRAUN). $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ (Aldrich) was stored under argon atmosphere and used without further purification. The solutions of BMIMBF₄ with 1 M $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ were prepared by adding appropriate amount of $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ to BMIMBF₄ in airtight flask inside glove box, and stirring the mixtures outside the box at 70 °C for several hours.

2.2. Measurement procedures and apparatus

All electrochemical experiments were conducted inside the argon filled glove box with water and oxygen below 1 ppm at room temperature. Cyclic voltammogram and pulse techniques were obtained using CHI660A electrochemical workstation (CH Instrument Co., USA) and electrodeposition experiments were accomplished with a DJS-292 potentiostat/galvanostat (Shanghai, China). A three-electrode electrochemical cell was used for the electrochemical experiments. The working electrode polished with a corundum suspension and rinsed with dry acetone before use, consisted of a platinum disk (geometric area = $3.14 \times 10^{-2} \text{ cm}^2$), nickel plate, stainless-steel plate, and Ag plate. The area of the working electrodes

except for Pt disk was determined separately in each experiment by visual inspection of the electrode surface after use and the area value can be controlled at approximately 0.1 cm^2 . Magnesium ribbon (1 mm diameter) was used as the counter electrode and platinum wire (0.5 mm diameter) as the quasi-reference electrode. The background cyclic voltammograms of the ionic liquid without magnesium salt were also examined.

Electrodeposition experiments were carried out on silver plate. The electroplated magnesium film was washed in the glove box with drying solvent without magnesium salt to remove the melt residue. Then, the samples were transferred out of the box and kept in sealing. The deposits were finally dried under vacuum. A Hitachi S-2150 scanning electron microscope (SEM) with an energy dispersive spectroscopy (EDS) was used to examine the surface topography and the element analysis of the electrodeposited film.

3. Results and discussion

Typical cyclic voltammograms that were recorded on the Pt disk electrode in BMIMBF₄ without (curve 1) and with 1 M $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ (curve 2) at a sweep rate of 50 mV/s are given in Fig. 1. The liquid itself exhibits an electrochemical window of above 4.2 V versus Pt RE. As shown in curve 2, a new cathodic peak A appears at -0.75 V , associated with an anodic peak A' located at about 0.25 V . Analysis of the deposit obtained under potentiostatic condition, by means of EDS analysis using the scanning electron microscopy, confirms the presence of metallic magnesium. Moreover, the corresponding anodic peak A' may be related to the dissolution process of magnesium, which is confirmed through the absence of magnesium by EDS analysis under potentiostatic condition. However, the dissolution peak A' is not a typical stripping peak of deposit, rather different from those in the high temperature molten salt system [6,8] or room temperature electrolyte system such as ethereal solutions of Grignard reagents (RMgX , where R = alkyl, aryl groups; X = halide: Cl, Br) [16–19], amidomagnesium halides [18], $\text{Mg}(\text{BR}_2\text{R}'_2)_2$ (R = alkyl and R' = aryl group) [16,18,19], and complexes of $\text{Mg}(\text{AX}_{4-n}\text{R}_n\text{R}'_n)_2$ (A = Al, B; X = Cl, Br; R,

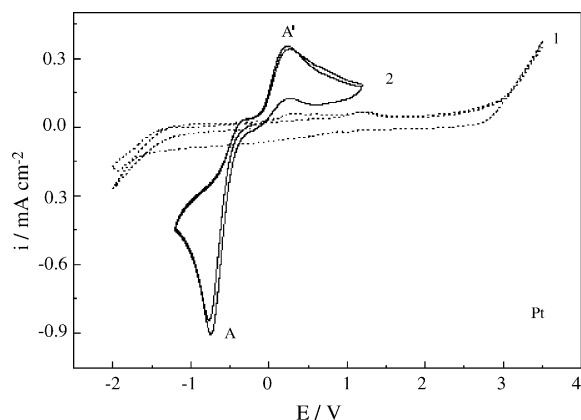


Fig. 1. Typical cyclic voltammograms of BMIMBF₄ without (curve 1) and with 1 M $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ (curve 2) on Pt disk electrode at 50 mV/s.

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