Electrochimica Acta 56 (2011) 6071–6077

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemistry of Zn(II)/Zn on Mg alloy from the *N*-butyl-*N*-methylpyrrolidinium dicyanamide ionic liquid

Ming-Jay Deng[a,*], Pei-Chiung Lin[b], Jeng-Kuei Chang[c,*], Jin-Ming Chen[a], Kueih-Tzu Lu[a]

[a] *National Synchrotron Radiation Research Center, Hsinchu, Taiwan*
[b] *Department of Chemistry, National Cheng Kung University, Tainan, Taiwan*
[c] *Institute of Materials Science and Engineering, National Central University, Taoyuan, Taiwan*

ARTICLE INFO

Article history:
Received 8 February 2011
Received in revised form 5 April 2011
Accepted 21 April 2011
Available online 3 May 2011

Keywords:
Electrodeposition
Ionic liquid
AZ91D
Zn
Corrosion
Dicyanamide

ABSTRACT

Electrochemical reaction of Zn(II)/Zn on glassy carbon electrode(GC) and Mg alloy substrates was investigated in the room-temperature ionic liquid, *N*-butyl-*N*-methyl-pyrrolidinium dicyanamide (BMP-DCA) containing $ZnCl_2$ at 323 K. Amperometric titration experiments suggest that Zn(II) reacted with DCA anions forming $[Zn(DCA)_3]^-$ complex anion, which also could be reduced to Zn metal via a single-step electron transfer process. By chronoamperometric measurements, the electrodeposition of Zn on GC and Mg alloy substrates involved three-dimensional instantaneous nucleation under diffusion control at 323 K. The Zn deposits are also systematically characterized by the techniques of powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Zn layer deposited at a lower current density on Mg alloy substrates was more compact and uniform when compared to that deposited at a higher current density; consequently, this coating revealed a protection capability for the Mg substrate against corrosion.

1. Introduction

Zn and Zn-based alloys are widely used as corrosion protective coatings for steel. Zn–Ni, Zn–Co and Zn–Fe have received the most attention and industrial interest [1,2]. By comparison, there is a few investigation of Zn and its alloys onto Mg alloys [3–5] although it has been reported that Zn and it alloys exhibit the high corrosion resistance [1,2]. In recent years, widespread use of Mg alloys to save weight in applications such as automobiles, aerospace, electronics, etc. however, these materials exhibit poor corrosion resistance, thereby limiting their usage in hostile environments. It necessitates the successful application of appropriate protective coatings, which can withstand service conditions. One of the coating technologies, which is claimed to be successfully applied for magnesium is electroplating. Though, Mg and its alloys have been classified as difficult to electroplate [6] because of: (1) rapid corrosion attack on Mg substrates by aqueous electrolytes, (2) high reactivity of Mg which rapidly forms loose immersion layers on the surface by replacement, which inhibit successive electrodeposition, and (3) rapid formation of MgO and/or $Mg(OH)_2$ film, as soon as the Mg is exposed to air or water, which prevent adhesion of the electrodeposited layers [6,7]. Consequently, Mg and its alloys are considered to be water sensitive substrates, and thus the importance of ionic liquids as non-aqueous electrolytes in electrodeposition.

In recent year, Prof. Endres et al. showed that the corrosion of Mg can be studied by in situ AFM. There were passivation phenomena in pure ionic liquids [8]. Therefore, aprotic ionic liquids (or molten salts) should be more appropriate electrolytes for the electrodeposition of Zn and its alloys since ionic liquids usually provide a wide working potential range, wide working temperature range, and good conductivity for electrolysis without hydrogen evolution. The electrodeposition of Zn in ionic liquid has been mainly studied in acidic chloroaluminate or chlorozincate ionic liquids with certain organic chlorides such as 1-ethyl-3-methylimidazolium (EMIC) or *N*-butyl-*N*-methylpyrrolidinium chloride (BMPC) [4,9–13] except the choline chloride-urea eutectic [3,14]. Their high moisture sensitivity, however, may complicate the incorporation of these ionic liquids into commercial devices. The applications of the ionic liquids has been greatly accelerated by the discovery of the landmark air- and water-stable ionic liquids. Recently, the most popular water-stable ionic liquids are those containing anions such as CF_3SO_3 and bis(trifluoromethylsulfonyl)imide ($TFSI^-$) [15–17]. However, previous studies indicated that $ZnCl_2$ is soluble in chloroaluminates [3,9,17] and chlorozincates ionic liquids [10–13,17], it is insoluble in the TFSI-based ionic liquids [17,18], and Zn(II) needs be introduced to the TFSI-based ionic liquids by anodic dissolution of Zn metal [18] or by dissolution of a Zn-TFSI salt

---

* Corresponding author. Fax: +886 3 578 3813.
E-mail addresses: martinez730523@yahoo.com.tw (M.-J. Deng), jkchang@ncu.edu.tw (J.-K. Chang).

0013-4686/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2011.04.082

prepared in advance because of the very weak Lewis base nature of the anions.

Liquids with the dicyanamide ion (DCA^-) are more practical solvents for electrodeposition of various metals including Zn since these ionic liquids are stable against moisture with water. In view of the good donor ligand property that is known for the dicyanamide anion [19,20], transition metal compounds should be soluble in the DCA-based ionic liquids by forming metal-DCA complex anions. To prepare an electrodepositing bath, therefore, becomes more convenient if DCA-based ionic liquids are used. Among the DCA^- based ionic liquids, the system containing 1-ethyl-3-methylimidazolium (EMI^+) and 1-butyl-1-methylpyrrolidinium (BMP^+) received much attention because of their low melting point and high solubility of transition metal halides [20]. From these electrolytes, some metals have been electrodeposited successfully [20–25]. Therefore, the system BMP^+ containing DCA^- only has been electrodeposited Mn [26] and Ag [27]. By comparison, BMP-DCA ionic liquid shows a wider cathodic potential window than EMI-DCA ionic liquid, it was chosen for electrodeposition of the more reactive metals [20]. According to the previous literatures, the grain size of the deposit in the nanometer regime from BMP^+ was much smaller than those obtained from EMI^+, which was in the micrometer range [28,29]. Dense and adherent deposit of Al in BMP-TFSI ionic liquid is an example [28,29]. Above of all, the BMP-DCA ionic liquid is likely a better choice to investigate the electrochemistry of Zn onto Mg alloys.

To the authors' knowledge, electrodeposition onto Mg alloy substrates in ionic liquids has only a few studied [3–5,30–32], especially Zn [3,5]. Good recycling of the overall materials can be maintained because Zn is a primary alloy element for the AZ series of Mg alloys. The present paper aimed to show the voltammetric and nucleation behaviors of Zn deposition at glassy carbon electrode (GC) and Mg alloy substrates. In this paper, titration experiments revealed that $ZnCl_2$ reacted with DCA^- forming the $[Zn(DCA)_3]^-$ complex anion which could be electrochemically reduced to Zn metal. Electrodeposits of Zn were prepared using controlled potential electrolysis at Mg alloy substrates and examined by powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In addition, the resulting corrosion resistance of the Zn-coated Mg alloy substrates was evaluated.

2. Experimental

2.1. Apparatus

All electrochemical experiments were performed under a purified nitrogen atmosphere in a glove box (Vacuum Atmospheres Co.), where both the moisture and oxygen contents were maintained below 1 ppm. The electrochemical experiments were accomplished with an AUTOLAB potentiostat/galvanostat controlled with the GPES software. Electrochemical experiments were performed in a three-electrode cell. The working electrodes were glassy carbon electrode (GC) and Mg alloy substrates. A platinum wire immersed in a ferrocene/ferrocenium ($Fc/Fc^+ = 50/50$ mol%) BMP-TFSI solution contained in a glass tube with porous Vycor tip (Bioanalytical Systems, MF-2042) was used as the reference electrode. The counter electrode was a spiral Zn wire which was separated from the bulk ionic liquid by a glass frit. Electrodeposition experiments were conducted on Mg alloy and graphite substrates.

The surface morphology and elemental composition of the Zn coatings were investigated with a Philip XL-40FEG field-emission SEM and a Hitachi Model HF-2000 field-emission TEM. The crystal structure of the Zn coatings was analyzed by a Rigaku D/MAX 2500 X-ray diffractometer. Several samples of deposited Zn were dissolved in 2 M nitric acid and standard method was employed to determine the quantity of Zn deposits with an atomic absorption spectroscope (AAS, SOLAAR M6). Deaerated 3.5 wt% NaCl solution was employed for electrochemical measurements. A platinum sheet and a Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. For a potentiodynamic polarization test, the potential was scanned from −1.6 to +0 V with a sweep rate of 1 mV/s.

2.2. Chemicals

The BMP-TFSI and BMP-DCA ionic liquids were prepared and prepared by following the previous literature [20,26,27,33]. The ILs were mixed with acetone and dichloromethane sequentially and filtrated to remove NaCl precipitates and vacuum dried at 393 K. It should be noted that NaCl and chloride impurities may be difficult to be completely removed from the liquids with DCA^-. The residual water contents of ionic liquids were measured by Karl Fisher titrator, and found to be less than 100 ppm. Anhydrous $ZnCl_2$ (99.99%, Aldrich), Zn wire (99.99%, Alfa Aesar), platinum wire (99.95%, Alfa Aesar) and a diecast AZ91D Mg alloy with 9.02 wt% Al and 0.49 wt% Zn was used in this study. Before electrodeposition, each sample was ground with SiC papers to a grit of 1200 in the glove box. The typical exposed area was 0.1 cm^2 with the other portion sealed with a Teflon film.

3. Results and discussion

3.1. Voltammetric studies

Fig. 1(a) shows that the blank BMP-DCA ionic liquid exhibit a cathodic potential limit near −3.4 V, and anodic potential limit near +1.1 V (vs. Fc/Fc^+). Stationary cyclic voltammogram and Linear sweep voltammogram that were recorded at GC and Mg alloy electrodes in the BMP-DCA ionic liquid containing 0.1 M $ZnCl_2$ at 323 K are also given in Fig. 1(b) and (c), respectively. The reduction of Zn(II) to Zn(0) at GC electrode occurs near −1.75 V and also requires a nucleation overpotential as clearly indicated by the presence of the "nucleation loop" in the voltammograms during the cathodic scan, and a sharp oxidation wave during the anodic scan. Such current loop is indicative of an overpotential driven nucleation/growth process that usually associated with the electrodeposition of a metal on a foreign substrate. The integrated

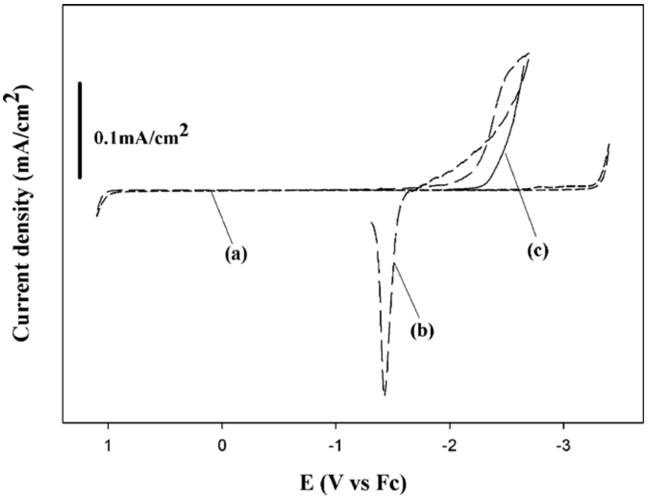

Fig. 1. Staircase cyclic voltammograms recorded at a glassy carbon electrode at 323 K (a) in blank BMP-DCA, (b) for 0.1 M Zn(II) in BMP-DCA ionic liquid, and (c) Staircase Linear scan voltammograms recorded at a Mg alloy electrode at 323 K for 0.1 M Zn(II) in BMP-DCA ionic liquid. The scan rate was 50 mV/s.