Effect of Electrolytes on Electrochemical Properties of Magnesium Electrodes

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ABSTRACT :

Magnesium (Mg) deposition and dissolution behaviors of 0.2 M $\text{MgBu}_2\text{-(AlCl}_2\text{Et)}_2$, 0.5 M $\text{Mg(ClO}_4)_2$, and 0.4 M $\text{(PhMgCl)}_2\text{-AlCl}_3$ -based electrolytes with and without tris(pentafluorophenyl) borane (TPFPB) are investigated by ex situ scanning electron microscopy (SEM) and galvanostatic cycling of Mg/copper (Cu) cells. To ascertain the factors responsible for the anodic stability of the electrolytes, linear sweep voltammogrammetry (LSV) experiments for various electrolytes and solvents are conducted. The effects of TPFPB as an additive on the anodic stability of 0.4 M $\text{(PhMgCl)}_2\text{-AlCl}_3/\text{THF}$ electrolyte are also discussed.

Keywords : Anodic limit, Electrolyte, Magnesium deposition, Magnesium dissolution, Scanning electron microscopy

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1. Introduction

Rechargeable magnesium (Mg) batteries are one of the most promising energy storage devices because the Mg anode offers potential advantages such as high specific capacities (3832 mAh cm^{-3} and 2230 mAh g^{-1}), negative reduction potential (-2.356 V vs. standard hydrogen electrode), and abundance in the earth's crust.¹⁻⁴⁾ Despite these advantages, the practical application of Mg batteries is quite challenging, because rechargeable Mg batteries suffer from poor cycling performance of the Mg negative electrode due to its passivating characteristics. The Aurbach group reported that Mg deposition is very difficult in most nonaqueous organic electrolytes because the surface species formed on Mg electrodes are electronically insulating (which leads to passivation of the electrode)

and do not assist the migration of Mg ions to the Mg electrode surface.⁵⁾ It is hence very important to find suitable electrolytes for rechargeable Mg batteries: specifically, reversible Mg deposition and dissolution, high ionic conductivity, and wide electrochemical windows should be attainable. It is known that the Mg electrode shows highly reversible behavior in a family of electrolyte solutions based on organohaloaluminate Mg salts, $\text{Mg(AlCl}_{4-x}\text{R}_y\text{R}'_z)$ ($\text{R}, \text{R}' = \text{alkyl or aryl groups}, x = y + z$), in tetrahydrofuran (THF).^{1,6)} However, the anodic stability of organohaloaluminate Mg salt/THF electrolytes limits the choice of cathodes. It was recently reported that electrolyte properties govern the choice of cathodes, and there is strong demand for the development of novel electrolyte systems showing a high anodic limit.⁴⁾ A Lewis acid as an anion receptor can interact with salt anions and mitigate oxidative decomposition of anions.⁷⁻⁹⁾ Accordingly, the anodic limit of electrolytes is expected to be shifted to high potential by the addition of anion

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receptors with electron deficient atoms.

Herein, we present the effects of various electrolyte systems on Mg deposition and dissolution. In addition, the role of tris(pentafluoro phenyl) borane (TPFPB) as an anion receptor in the anodic stabilities of electrolytes and the cycling properties of Mg/Mo₆S₈ cells with 0.4 M (PhMgCl)₂-AlCl₃/THF is discussed.

2. Experimental

2.1. Materials

Electrolytes comprising tetrahydrofuran (THF) solvent and complexes of MgBu₂-(AlCl₂Et)₂ were prepared by the dropwise addition of 1 M ethylaluminumdichloride (EtAlCl₂) in hexane (Aldrich) to a vigorously stirred 1M dibutylmagnesium (Bu₂Mg) in heptanes (Aldrich).^{6,10} An exothermic reaction took place, yielding a powdery white precipitate. The reaction was allowed to continue at room temperature for 48 h in a glove box filled with argon. The resulting white powder was obtained after drying in a vacuum at room temperature for 10 h. The THF solvent distilled with a sodium-benzophenone complex was added to the dry white solid, MgBu₂-(AlCl₂Et)₂. The solution was clear and colorless.

0.5 M AlCl₃ in THF solution (Aldrich, 99.9%) was slowly added dropwise to a predetermined quantity of 2 M phenylmagnesiumchloride (PhMgCl)/THF solution (Aldrich) at 0°C. The resulting solution, 0.4 M (PhMgCl)₂-AlCl₃ in THF, was stirred for an additional 16 h at room temperature.¹¹ 0.5 M Mg(ClO₄)₂ (Aldrich) dissolved in propylene carbonate (PC)/dimethyl carbonate (DMC) (50/50, v/v) (Soulbrain Co. Ltd.) mixed solvent or acetonitrile was then prepared. 1 wt.% tris(pentafluorophenyl) borane (TPFPB) (Aldrich) as an additive was added into 0.4 M (PhMgCl)₂-AlCl₃/THF electrolyte.

2.2. Electrochemical measurements

The anodic limits of the electrolytes were determined by means of linear sweep voltammetry at a scan rate of 20 mVs⁻¹ using an Iviumstat (Ivium Technologies, The Netherlands); we used stainless steel as the working electrode and a magnesium electrode as the reference and counter electrodes. All of the electrodes were polished with sandpaper and rinsed with dry THF prior to use.

To investigate the electrochemical reversibility of Mg deposition and dissolution in various electrolyte

systems, cycling experiments for Mg/Cu cells were galvanostatically conducted at a rate of C/20 (0.163 mA cm⁻²) using a computer-controlled battery measurement system (WonATech WBCS 3000). Cu functioned as the working electrode and a Mg disc as the counter electrode.

2.3. Scanning electron microscopy observations

After rinsing the electrodes in THF or acetonitrile solvent, the surface morphology changes of the Mg electrode and Cu substrate after Mg deposition and dissolution were observed using a field emission scanning electron microscope (FE-SEM; JEOL JSM-6700F). During the acquisition of the images, an energy dispersive spectrometer (EDS) was also used to determine the types of chemical components of electrodeposited Mg on a Cu foil and Mg electrode after Mg dissolution.

3. Results and Discussion

Fig. 1 shows the galvanostatic cycling of Mg/Cu cells in various electrolytes. 1% of the magnesium from the Mg electrode was utilized and the capacity was 3.25 mAh cm⁻². The initial steep potential drop indicating very difficult Mg dissolution at the Mg electrode is observed and then, the potential is shifted toward 0 V. This indicates that once the Mg dissociation from the Mg electrode is initiated, further Mg dissolution at the Mg electrode and Mg deposition at the Cu substrate readily take place. 0.2 M MgBu₂-(AlCl₂Et)₂/THF electrolyte exhibited a large potential drop during the first Mg deposition and the overpotential for further Mg deposition discernibly decreased. It is thought that 0.2 M MgBu₂-(AlCl₂Et)₂/THF electrolyte is prone to oxidize on the Mg electrode during Mg dissolution and results in the formation of a surface layer that suppresses re-deposition of Mg onto the Mg electrode. Indeed, slightly increased potential for repeated Mg deposition and dissolution was observed due to ohmic resistance of the resistive surface layer, as shown in Fig. 1(a). 0.5 M Mg(ClO₄)₂ in acetonitrile showed a very high potential for the Mg dissolution from the Mg electrode and the Mg deposition on a Cu substrate, and a sharp potential rise during the next Mg dissolution from the Cu substrate with Mg deposition in Fig. 1(b). This significantly increased potential during the first Mg dissolution may lead to Cu dissolution from a Cu substrate. This agrees well with a previous

Fig. 1. Galvanostatic cycling performance of Mg/Cu cells at a rate of C/20 in (a) 0.2 M $\text{MgBu}_2\text{-(AlCl}_2\text{Et)}_2/\text{THF}$, (b) 0.5 M $\text{Mg(ClO}_4)_2$ in acetonitrile, (c) $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$, (d) $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ with 1% TFPFB.

Fig. 2. SEM images and EDS spectra for (a) Mg deposit on a Cu substrate, (b) Mg electrode after Mg dissolution in 0.2 M $\text{MgBu}_2\text{-(AlCl}_2\text{Et)}_2/\text{THF}$. Red box represents the selected zone for the EDS measurements.

report that Mg electrode is mostly blocked by the resistive surface layer, and Mg deposition is extremely inhibited.⁵⁾ It is known that reversible Mg deposition is prohibited in aprotic solvents containing a commercial ionic salt such as $\text{Mg(ClO}_4)_2$.^{4,12,13)} 0.4 M $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ with and without tris(pentafluorophenyl) borane (TFPFB) electrolytes exhibited a relatively low potential drop for Mg deposition at the Cu substrate and highly stable potential behavior for Mg deposition and dissolution on a Cu substrate, as presented in Figs. 1(c) and (d). It is clear that 0.4 M $(\text{PhMgCl})_2\text{-AlCl}_3$ in THF forms a less resistive surface film and

effectively assists Mg deposition and dissolution during cycling. TFPFB as an additive did not lead to a large potential drop for Mg deposition at the Cu substrate and a high potential rise for Mg dissolution.

SEM images for magnesium (Mg) deposition on a Cu substrate and Mg dissolution from a magnesium electrode in 0.2 M $\text{MgBu}_2\text{-(AlCl}_2\text{Et)}_2/\text{THF}$ electrolyte are shown in Fig. 2. The deposition rate was 0.163 mA cm^{-2} with a capacity of 6.5 mAh. The morphological measurements exhibited that Mg deposition from 0.2 M $\text{MgBu}_2\text{-(AlCl}_2\text{Et)}_2/\text{THF}$ electrolyte is very uniform. It is known that the identity of the electrolyte

affects the morphology of Mg deposition.¹⁴⁾ Pyramid-shaped Mg deposition without dendritic formation is important for practical application. The EDS results confirmed that the deposits on a Cu substrate are pure Mg without any surface species, as presented in Fig. 2(a). As clearly seen in Fig. 2(b), the Mg electrode had a very coarse surface and many voids after Mg dissolution. Importantly, aluminum (Al) and oxygen (O) signals appeared in the EDS spectra obtained from the magnesium electrode after Mg dissolution. The Al signal is attributed to compounds formed via the decomposition of the anion species, AlCl_3Et^- , in the electrolyte solution. It is clear that the 0.2 M $\text{MgBu}_2\text{-(AlCl}_2\text{Et)}_2/\text{THF}$ electrolyte electrochemically decomposes and produces the surface species at the Mg electrode during Mg dissolution.

Fig. 3 displays SEM images and EDS spectra for the Cu substrate after Mg deposition and the Mg electrode after Mg dissolution in 0.5 M $\text{Mg}(\text{ClO}_4)_2$ in acetonitrile, respectively. In addition, SEM images and EDS spectra for the Mg electrode after Mg deposition are shown in Figs. 3(e) and (f). The EDX spectrum of Mg deposits on a Cu electrode in 0.5 M $\text{Mg}(\text{ClO}_4)_2$ in acetonitrile shows peaks corresponding to chlorine (Cl), O, and Mg signals, as seen in Fig. 3(a). The Cl and O signals are attributed to compounds formed via the decomposition of ClO_4^- anions in Fig. 3(a) and are not observed for the Cu substrate, as shown in Fig. 3(b). This indicates that significant decomposition of ClO_4^- anions takes place along with Mg deposition on the Cu substrate. Similarly, atomic amounts related to Cl, O, and Mg are detected in the EDX spectrum during Mg

Fig. 3. SEM images and EDS spectra for (a), (b) Mg deposit on a Cu substrate, (c), (d) Mg electrode after Mg dissolution, (e), (f) Mg re-deposit on Mg electrode in 0.5 M $\text{Mg}(\text{ClO}_4)_2/\text{acetonitrile}$.

Fig. 4. SEM images and EDS spectra for Mg deposits on Cu substrates in (a) $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$, (b) $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ with 1% TFPFB. SEM images and EDS spectra for Mg electrodes after Mg dissolution in (c) $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$, (d) $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ with 1% TFPFB.

dissolution from the Mg electrode, as shown in Fig. 3(c). It was reported that ClO_4^- anions react with the Mg electrode and Mg-Cl-O species are formed on the Mg electrode surface during storage for 3 h.⁵⁾ Importantly, non-uniform Mg dissolution from the Mg electrode occurred, as depicted in the inset of Fig. 3(d). Surprisingly, a thick surface layer entirely covered the Mg electrode when Mg dissolved from the Cu substrate with Mg deposition on the Mg electrode, as shown in Figs. 3(e) and (f). The EDX analysis revealed that this thick layer consists of Cu and O. It is concluded that a sharp potential rise during Mg dissolution from the Cu substrate with Mg deposition leads to Cu dissolution from the Cu substrate and causes irreparable damage to the Mg electrode. The EDS results of Figs. 4(a) and (b) confirmed that the deposits on the Cu substrate are pure Mg without any surface species. Interestingly, there is a significant difference between the SEM images obtained from Mg deposits in 0.4 M $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ with and without TFPFB. It is clear that the shape of the Mg deposit strongly depends on the electrolyte composition.

Fig. 5 presents typical linear sweep voltammetry (LSV) curves in various electrolytes and solvents. Stainless steel (SS), an important component in testing

coin cells, was used as a working electrode. The presence of the most oxidative species such as anions governs the anodic stability window of the electrolyte.¹¹⁾ 0.2 M $\text{MgBu}_2\text{-(AlCl}_2\text{Et)}_2/\text{THF}$ and 0.4 M $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ electrolytes, developed by Aurbach, display an electrochemical stability window of up to 2.75 V and 2.5 V vs. a Mg reference electrode on a SS working electrode, respectively. It should be noted that the anodic stability of electrolytes will be greatly different with working electrodes (platinum, copper, nickel, stainless steel, and aluminum). The onset potential of pure THF solvent is 0.2 V more positive than that of 0.2 M $\text{MgBu}_2\text{-(AlCl}_2\text{Et)}_2/\text{THF}$ electrolyte, as shown in Fig. 5. Since THF solvent without salt has a very high polarization resistance, it may lead to a very high overpotential. In this regard, higher oxidation potential of THF can be thought to attribute to its high polarization resistance. We think that this overpotential can make the oxidation of THF solvent more difficult on a stainless steel working electrode and the anodic stability of the electrolyte solution is governed by organochloroaluminate Mg salt rather than the THF solvent.¹⁵⁾ Fig. 5(b) displays a comparison between the anodic limits of 0.4 M $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ with and without 1% tris(pentafluorophenyl)phosphine.

Fig. 5. Linear sweep voltammograms depicting anodic stability of (a) various electrolytes and solvents, (b) $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ with and without 1% TFPFB.

nyl) borane (TPFPB). Interestingly, the oxidative stability of 0.4 M $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ with TFPFB on a SS working electrode reaches 2.9 V on the SS electrode. This implies that electron deficient boron atoms of TFPFB interact with the anion species such as Ph_4Al^- , Ph_3AlCl^- , $\text{Ph}_2\text{AlCl}_2^-$, and PhAlCl_3^- in the electrolyte and lessen the oxidative nature of the electrolyte.^{10,11} High oxidative stability of 0.4 M $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ with TFPFB, which is analogous with a THF solvent, is expected to ensure very good compatibility toward the cathode.

4. Conclusions

On the basis of galvanostatic cycling of Mg/Cu cells, highly reversible Mg deposition and dissolution processes were obtained in 0.4 M $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ electrolytes with and without TFPFB. The observation of surface morphology clearly showed that 0.2 M $\text{MgBu}_2\text{-(AlCl}_2\text{Et)}_2/\text{THF}$ decomposes during Mg dissolution and the shape of the Mg deposits is

affected by the electrolyte components. Linear sweep voltammetry experiments confirmed that the addition of the TFPFB Lewis acid could improve the anodic stability of 0.4 M $(\text{PhMgCl})_2\text{-AlCl}_3/\text{THF}$ electrolytes. We hope that the results of this study and the associated analysis contribute to the search for advanced electrolyte ensuring use of high voltage cathodes.

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