



High concentration magnesium borohydride/tetraglyme electrolyte for rechargeable magnesium batteries



Feilure Tuerxun^{a, b}, Yasen Abulizi^{a, b}, Yanna NuLi^{a, b, *}, Shuojian Su^{a, b}, Jun Yang^{a, b}, JiuLin Wang^{a, b}

^a School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

^b Hirano Institute for Materials Innovation, Shanghai Jiao Tong University, Shanghai 200240, PR China

HIGHLIGHTS

- A magnesium battery electrolyte based Mg(BH₄)₂ in TG with high safety is developed.
- Mg(BH₄)₂ in TG shows an improved performance than in DME and DGM reported before.
- The electrolyte based on Mg(BH₄)₂ in TG has higher concentration than in DME and DGM.
- The solution shows 2.4 V stability on SS, near 100% deposition/dissolution efficiency.
- Good compatibility with Mo₆S₈ cathode confirms the application in Mg batteries.

ARTICLE INFO

Article history:

Received 1 September 2014

Received in revised form

21 November 2014

Accepted 25 November 2014

Available online 27 November 2014

Keywords:

Deposition and dissolution

Electrochemical reversibility

Magnesium

Electrolyte

Rechargeable magnesium batteries

ABSTRACT

High concentration magnesium borohydride/tetraglyme electrolyte for rechargeable magnesium batteries is simply prepared by dissolving inorganic magnesium salt Mg(BH₄)₂ in tetraglyme (TG) ether solvent with good safety. 90 °C heating treatment is performed in the preparation process and LiBH₄ as a chelating agent is added to improve the electrochemical performance. Mg deposition–dissolution performance and the electrochemical window of the electrolyte on non-inert stainless steel (SS), nickel (Ni), copper (Cu) electrodes and inert platinum (Pt) electrode are systematically studied by cyclic voltammetry and constant current discharge–charge measurements. 0.5 mol L⁻¹ heated Mg(BH₄)₂/LiBH₄/TG ([LiBH₄] = 1.5 mol L⁻¹) solution shows good electrochemical performance with 2.4 V (vs. Mg RE) anodic stability on stainless steel, close to 100% Mg deposition/dissolution efficiency and high cycling reversibility. Furthermore, the reversible electrochemical process of Mg intercalation into Mo₆S₈ cathode with excellent cycling performance in the electrolyte indicates the feasible application in rechargeable magnesium batteries.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The demand for green rechargeable batteries for applications such as electric vehicles and large scale power storage systems is constantly increasing because of fossil energy shortage and environmental issues. Following the rapid development of electric automobiles, batteries are now needed to have not only high energy density, but also high power density and good safety. Rechargeable magnesium batteries with magnesium as the anode may be a

potential candidate comparable with post Li-ion batteries containing a lithium metal anode due to a relatively low price (\$2700/ton and \$64,800/ton for Mg and Li, respectively), a high theoretical volumetric capacity (3832 mAh cm⁻³ for Mg and 2062 mAh cm⁻³ for Li) and a higher expected safety (less dendritic morphologies for magnesium deposits than lithium) for magnesium compared with lithium [1,2].

Different from Li batteries, Mg batteries suffer from the lack of suitable cathode materials and electrolyte systems. In many nonaqueous solutions, a reversible process of electrochemical Mg deposition–dissolution is hard achieved because of the formation of compact passive film [3–6]. Therefore, it is necessary to discover a right electrolyte with reversible Mg deposition and a wide

* Corresponding author. School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China.

E-mail address: nlyn@sjtu.edu.cn (Y. NuLi).

electrochemical window for the development of magnesium batteries. The significant progress is the 0.25 mol L⁻¹ Mg(AlCl₂BuEt)₂/THF (Bu = butyl, Et = ethyl) electrolyte and 0.4 mol L⁻¹ (PhMgCl)₂-AlCl₃/THF electrolyte proposed by Aurbach et al., which have high anodic stability (2.5 V and 3.3 V vs. Mg RE on inert Pt electrode, respectively) and Mg electrodes behave highly reversibly in them [7–11]. In 2011, Kim et al. reported firstly the non-nucleophilic electrolyte based on the crystal of [Mg₂Cl₃-6THF][HDMSAlCl₃] for reversible magnesium deposition–dissolution [1]. Recently, a family of novel boron based electrolytes with high ionic conductivity, excellent Mg deposition reversibility as well as high anodic stability were proposed [12,13]. On the other hand, our group reported a new phenolate-based electrolyte, which exhibits air insensitive character and excellent magnesium deposition–dissolution performance [14]. However, these electrolytes are generally composed of organic magnesium salts and may corrode non-inert current collectors duo to the presence of halides in the cation and anion components of the electrolytes, although some of these electrolytes show impressive stability against electrochemical oxidation [12,15]. Hence, it is still necessary to find electrolytes with high stabilities on non-inert current collectors for the realizing a practical rechargeable Mg battery system.

Recently, Mohtadi et al. [16] confirmed reversible magnesium deposition–dissolution from a new class of electrolytes based on a relatively ionic and halide-free inorganic salt Mg(BH₄)₂ in both tetrahydrofuran (THF) and dimethoxyethane (DME) ether solvents. LiBH₄ was employed as an additive to increase the electrochemical performance, and 94% coulombic efficiencies for Mg deposition–dissolution were observed. Y.Y. Shao et al. [17] further developed Mg(BH₄)₂ based electrolyte with diglyme (DGM) as the solvent and LiBH₄ also the additive, in which the coulombic efficiency of close to 100% was achieved in the electrolyte of 0.1 mol L⁻¹ Mg(BH₄)₂/LiBH₄/DGM ([LiBH₄] = 1.5 mol L⁻¹). The research about the structure–property relationship showed that the coulombic efficiency in Mg(BH₄)₂-based electrolyte increases according to the series THF < DME < DGM because of the improved stability of the solvated Mg(BH₄)₂ complexes with the denticity of the solvent ligands (monodentate, bidentate, and tridentate, respectively). However, the solubility of Mg(BH₄)₂ in DGM and DME is 0.1 M/0.01 mol L⁻¹ with/without LiBH₄ respectively. [17] The limited concentration of Mg(BH₄)₂ in solvents will lead to the limited rate performance of Mg batteries for practical application. Herein, quinquedentate ligand tetraglyme (TG) with higher safety (the boiling/flash points of TG, DGM, DME and THF are 275 °C/141 °C, 162 °C/57 °C, 85 °C/–2 °C and 66 °C/–14 °C, respectively) was further developed as the solvent of Mg(BH₄)₂. More importantly, a high concentration electrolyte based on Mg(BH₄)₂ in TG with a higher anodic stability on non-inert metal electrode was pursued for practical application.

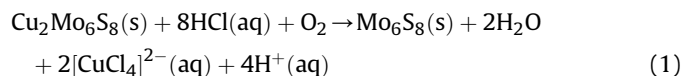
2. Experimental

2.1. Chemicals and material synthesis

Magnesium borohydride (Mg(BH₄)₂, 95%) and magnesium ribbon (1 mm diameter) were purchased from Sigma–Aldrich. Lithium borohydride (LiBH₄, 95%) was purchased from J&K Scientific. Tetrahydrofuran (THF), dimethoxyethane (DME), diglyme (DGM) and tetraglyme (TG) were purchased from Aladdin reagent and further dried using 3 Å molecular sieve.

The synthetic work was conducted in an argon-filled glove box (Mbraun, Unilab, Germany) containing less than 2 ppm H₂O and O₂. The electrolytes were prepared by dissolving the predetermined amount of Mg(BH₄)₂ and LiBH₄ in solvents under stirring at room temperature or 90 °C for at least 2 h.

Synthesis route of Mo₆S₈ followed the literature [18]. In briefly, the mixture of 1 g MoS₂ (99%, Aldrich), 0.398 g CuS (99.5%, Cerac), 0.602 g Mo (99%, Aldrich) and 4 g KCl (99%, Aldrich) was pestled for over 10 min and then heated at 850 °C for 60 h. The product was washed by deionized water and sonicated to obtain Cu₂Mo₆S₈. Then, Mo₆S₈ was prepared by chemical removal of the copper from Cu₂Mo₆S₈ using an aqueous HCl solution through the following reaction:



2.2. Measurement procedures and apparatus

Cyclic voltammograms (CVs) were conducted in three-electrode cells inside an argon-filled glove box using an electrochemical instrument of CHI604A Electrochemical Workstation (Shanghai, China). The working electrode was a stainless steel, nickel, copper and platinum disk (geometric area = 3.14 × 10⁻² cm²), which was polished with a corundum suspension and rinsed with dry acetone before use, and magnesium ribbon as counter and reference electrodes. Electrochemical magnesium deposition–dissolution cycles were examined with CR2016 experimental coin cells on a land battery measurement system (Wuhan, China). Stainless steel foil (Φ12 mm) was served as the working electrode (substrate). Mg disc as the counter electrode. An Entek PE and a fiber membrane as the separator. The cells were assembled in the glove box. Magnesium was deposited onto the stainless steel substrate for fixed periods of 30 min followed by stripping to a fixed potential limit of 0.8 V vs. Mg at a constant current density of 0.088 mA cm⁻². There was a 30 s rest between deposition and dissolution. The magnesium deposition and dissolution on the substrate were referred to as the discharge and charge process, respectively. The time of charge divided by the time of discharge was defined as the deposition–dissolution efficiency.

The Mo₆S₈ electrode was prepared by casting and pressing a 8:1:1 weight-ratio mixture of Mo₆S₈, super-P carbon powder and polyvinylidene fluoride (PVDF) binder dissolved in N-methyl-2-pyrrolidinone (NMP) onto stainless steel current collector followed by drying in vacuum at 120 °C. CR2016 coin cells were fabricated using Mo₆S₈ cathode, Mg disc anode, Entek PE and fiber membrane separator, and 0.5 mol L⁻¹ heated Mg(BH₄)₂/TG or Mg(BH₄)₂/LiBH₄/TG ([LiBH₄] = 1.5 mol L⁻¹) electrolyte. The charge–discharge tests of the coin cells were carried out on the land battery measurement system with the cutoff voltage of 1.6/0.5 V vs. Mg.

IR analysis of the solutions was run using a Spectrum 100 FT-IR spectrometer (Perkin Elmer, Inc., USA). Nuclear magnetic resonance (NMR) measurements were performed using a Bruker Avance 400 MHz spectrometer equipped with a CP/MAS probe. The spectra were reported in part per million (ppm) with referenced to tetramethylsilane (TMS) and BF₃·O(CH₂CH₃)₂ as the external standards of ¹H and ¹¹B, respectively. X-ray diffraction (XRD) analysis of the magnesium deposits was conducted on a Rigaku diffractometer D/MAX-2200/PC equipped with Cu Kα radiation. The morphology of the deposits was observed using scanning electron microscopy (SEM) on a FEI SIRION200 field-emission microscope. Before the analysis of the deposits, the sample deposited for 10 h at 0.088 mA cm⁻² was washed in the glove box with drying THF solvent to remove soluble residue and then transferred out of the box and kept without exposure to the atmosphere.

Download English Version:

<https://daneshyari.com/en/article/1292937>

Download Persian Version:

<https://daneshyari.com/article/1292937>

[Daneshyari.com](https://daneshyari.com)