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Performance study of magnesium-polyaniline rechargeable battery in 1-ethyl-3-methylimidazolium ethyl sulfate electrolyte

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ABSTRACT

A novel electrolyte system for the magnesium-polyaniline rechargeable battery containing 0.025 M magnesium sulfate ($MgSO_4$) in 1-ethyl-3-methylimidazolium ethyl sulfate (EMIES) has been developed. The electrochemical properties of magnesium and polyaniline electrodes in the $MgSO_4$–EMIES solution are investigated, respectively. The results show that the corrosion potential of magnesium is −1.55 V (vs. SCE) in 0.025 M $MgSO_4$–EMIES and magnesium has high dissolution and deposition reversibility in the solution. Polyaniline shows good oxidation and reduction reversibility in 0.025 M $MgSO_4$–EMIES and the loose and porous structure of polyaniline is helpful to the doping and de-doping of anions as well as electron transfer. The study of the effect of current density on discharge capacity shows that the magnesium-polyaniline battery has higher discharge capacity at lower current density. At 667 mA g^{-1}, magnesium-polyaniline battery has an average discharge potential of 2.10 V and the first cycle discharge capacity could be 116 mAh g^{-1}. The magnesium-polyaniline battery has good cycle performance and the coulombic efficiency of the 60th cycle can be nearly 95%. The new cheap and simple magnesium-polyaniline battery is of great significance in the future rechargeable battery.

1. Introduction

With the increasing demand for energy, how to develop the rechargeable battery having the characteristics of high energy density, economy and environmental friendly has been one of the biggest challenges facing most electrochemical workers [1,2]. The currently widely used lithium ion battery has high voltage, high specific capacity and energy density. But not only lithium and lithium salts are of high cost, but also the organic electrolyte used is easy to burn or explode [3,4]. Therefore, it is urgent to find new types of batteries with greater safety and lower cost to meet the demand of gradually expanded market.

Magnesium is in the diagonal position of lithium in the periodic table of the elements so that it will have similar physical and chemical properties as lithium. It has negative electrode potential (−2.36 V vs. NHE) and high theoretical specific capacity (2205 mAh g^{-1}). In addition, magnesium has lower reactivity than lithium, which will make it much easier to operate than lithium. What's more, magnesium is of low cost and environmental friendly. Consequently, magnesium will be an attractive candidate for the anode material of the future rechargeable battery [5].

Polyaniline is a promising cathode material for polyaniline-based batteries like lithium-polyaniline [6,7], zinc-polyaniline [8,9] and lead dioxide-polyaniline batteries [10]. Polyaniline has reversible oxidation and reduction characteristics, high conductivity and good thermal stability [11–13]. Furthermore, it is environmental friendly and inexpensive. It has been reported that the polyaniline battery has good electrochemical reversibility and the specific capacity can be over 100 mAh g^{-1} [14,15]. The reaction mechanism of magnesium-polyaniline battery is shown in Fig. 1. The charge progress of magnesium-polyaniline battery corresponds to the reduction of Mg^{2+} and the oxidation of polyaniline accompanied by the doping process of protons and anions $SO_4{}^{2-}$ to the polyaniline structure. On the contrary, the discharge one could be the oxidation of anode magnesium and the reduction of cathode polyaniline as well as the de-doping process of polyaniline. The reaction progress is similar to the reported lead dioxide-polyanline battery [10], magnesium-polyaniline [16] or zinc-polyaniline battery [17].

The study of magnesium battery has developed rapidly since Aurbach et al. [18] made a complete magnesium rechargeable battery in 2000. As magnesium is relatively active, it can form dense passivation films in the aqueous and some non-aqueous media. Therefore, how to realize the reversible deposition of magnesium is a severe problem to be solved. It is reported that magnesium can achieve reversible deposition in ethereal solutions of Grignard

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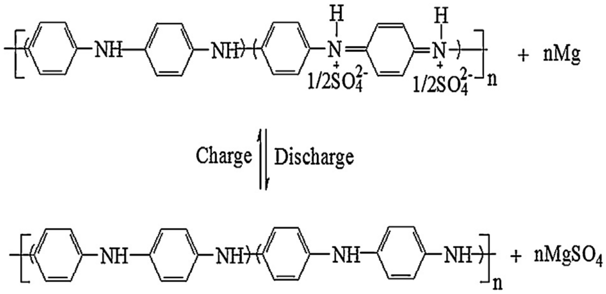

Fig. 1. The reaction mechanism of magnesium-polyaniline battery.

reagents RMgX (R = alkyl, aryl groups; X = halide: Cl, Br) [19,20], amid magnesium halides, $Mg(BR_2R'_2)_2$ (R = alkyl and R′ = aryl group) [21,22], and complexes of $Mg(AX_{4-n}R_{n'}R'_{n''})_2$ (A = Al, B, As, P, Sb; X = Cl, Br, F; R, R′ = alkyl or aryl groups, and $0 < n < 4$, $n' + n'' = n$) [23]. However, these processes will be complicated by the adsorption-desorption processes of the species in addition to the simple oxidation and reduction of magnesium [24]. Although the magnesium battery in aqueous solution has been reported by Kumar et al. [16] and Kong et al. [25], the battery is much more difficult to keep stable because magnesium is very active in the aqueous solution. Therefore, it is necessary to find a suitable electrolyte for the future magnesium battery.

Ionic liquid known as room-temperature molten salts has many excellent characteristics such as lower vapor pressure, wide electrochemical window, non-flammability, good thermal and electrochemical stability [26–28]. Accordingly, it has been acknowledged as the next generation electrolyte for the rechargeable battery. Hsiu et al. [29] has reported that there is the underpotential deposition of zinc on Pt and Ni electrodes in EMIC (1-ethyl-3-methylimidazolium chloride). The ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate (EMIES) has a wide electrochemical window of 3.80 V (−2.40 to 1.40 V). Therefore, ionic liquid EMIES may have good application prospects in the rechargeable battery.

In this paper, the ionic liquid EMIES is adopted as a novel electrolyte for the magnesium-polyaniline battery with $MgSO_4$ as the dissolved salts. The appropriate concentration of $MgSO_4$ was first investigated. Then we described the electrochemical properties of magnesium and polyaniline electrodes in the $MgSO_4$–EMIES electrolyte by varied electrochemical methods. The morphologies of

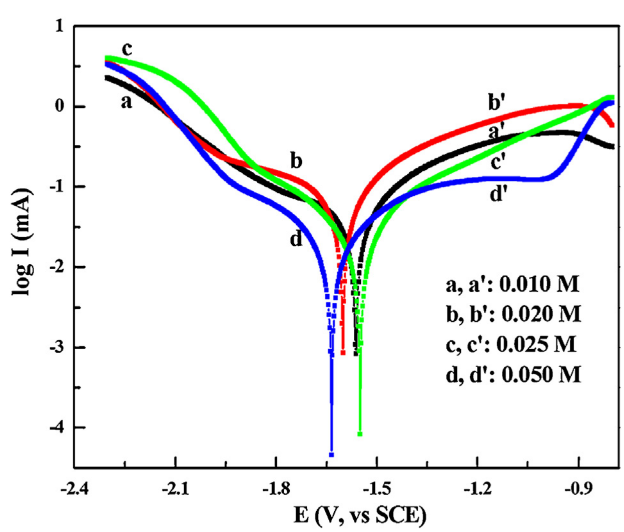

Fig. 2. Slow potentiodynamic polarization curves of magnesium in different concentration of $MgSO_4$–EMIES.

magnesium and polyaniline were characterized as well. And the charge and discharge behavior of the magnesium-polyaniline battery was investigated.

2. Experimental

2.1. Reagents and materials

The magnesium (99.9%) was purchased from Futai Metal Materials Co., Ltd (China). N-methylimidazole (99.5%) was from Nuotai Chemical Co., Ltd. (China). All other chemicals such as aniline and magnesium sulfate anhydrous were of analytical grade from Sinopharm Chemical Reagent Co., Ltd. The aniline was distilled under reduced pressure prior to use.

1-Ethyl-3-methylimidazolium ethyl sulfate (EMIES) was synthesized according to literatures [30,31]. Briefly, EMIES was synthesized by alkylation of N-methylimidazole with an excess of diethyl sulfate in toluene solution. After stirring in ice bath for 6 h, the production was washed by toluene for several times and dried in high vacuum at 75 °C until constant weight.

Magnesium (geometric area of $2\,cm^2$) was first polished by aluminum oxide cloth (No. 0120#) and metallographic abrasive paper (W20/02) and then washed with acetone. Polyaniline was electrochemically polymerized at constant current density of $0.25\,mA\,cm^{-2}$ on platinum (Pt) electrode for 1000 s in the 0.20 M aniline and 0.50 M H_2SO_4 mixed solution with 1/3 volume EMIES (with respect to aniline). After deposition, the polyaniline was first dried for 0.5 h and then washed successively with distilled water and ethanol. The polyaniline powder was dried under vacuum for 2 h at 70 °C and then used as the cathode for the electrochemical studies. Assuming 100% current efficiency during the polymerization of aniline, the mass of polyaniline sulphate could be calculated from the equations [14,15,32]:

$$m = \frac{jt(M_m + yM_a)}{(2+y)F}$$

where m is the mass of the polyaniline polymerized with current density j during the time t, M_m and M_a are the molar masses of the aniline monomer and inserted sulphate anions, respectively and $y = 0.5$ is the doping degree for the emeraldine salt. Hence the mass of the polyaniline on the Pt electrode calculated is about 0.15 mg. At the same time, we can approximately calculate the film thickness of the polyaniline on the Pt electrode by using the following equation:

$$d = \frac{m}{\rho A}$$

where d is the film thickness of the polyaniline polymerized on the Pt electrode, m is the mass of the polyaniline, ρ is the specific density of polyaniline ($1.14\,g\,cm^{-3}$ [33]), A is the geometric area of the Pt electrode ($2\,cm^2$). Therefore, the film thickness of polyaniline is calculated to be 0.66 μm.

2.2. Apparatus and methods

Slow potentiodynamic polarization, cyclic voltammetry (CV), chronoamperometry (I-t) and chronopotentiometry (E-t) tests were carried out by using an Autolab/PGSTAT 30 potentiostat/galvanostat equipment (Eco chemie, Netherlands) based on a three-electrode system with Pt-polyaniline ($2\,cm^2$) or magnesium ($2\,cm^2$) electrodes as the working electrode, Pt ($6\,cm^2$) as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The slow potentiodynamic polarization curves of magnesium were scanned from −2.3 V to −0.8 V with a scan rate of $5\,mV\,s^{-1}$ while the polarization curves of polyaniline were conducted from 0.80 V to 0.95 V at the same scan rate. The cyclic voltammetry of polyaniline was measured from 0.0 V to 1.35 V with increasing scan rate from $1\,mV\,s^{-1}$ to $20\,mV\,s^{-1}$.