



Effect of adding various carbon additives to porous zinc anode in rechargeable hybrid aqueous battery



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ARTICLE INFO

Article history:

Received 6 August 2015

Received in revised form

13 October 2015

Accepted 23 October 2015

Available online 27 October 2015

Keywords:

Carbon additive

Anode

Zinc

Hybrid

Aqueous battery

ABSTRACT

Anodic behavior of porous Zn in rechargeable hybrid aqueous battery is investigated. The battery comprises porous Zn anode and LiMn_2O_4 cathode. The electrolytes are Li^+ and Zn^{2+} of sulfate salt in aqueous solution. The initial discharge capacity of pure porous Zn is 114 mAh g^{-1} , and the capacity decreases to less than 59 mAh g^{-1} after 36 cycles. Then, the effects of various carbon additives on the battery performance are studied. The results show that the adding of active carbon increases the initial discharge capacity to 150 mAh g^{-1} , and the capacity maintains above 60 mAh g^{-1} even after 210 cycles. The reasons for improvement for the battery are investigated by Tafel, scanning electron microscopy, and X-ray Diffraction.

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1. Introduction

With the continuous deterioration of the environment and excessive consumption of fossil fuels, the development of renewable energy sources of power like wind and solar has attracted considerable attention [1,2]. The most vexing issues of renewable energy are the sheer variability and intermittent of wind and solar power. Thus, it is significant to develop an energy storage system to solve the issues. All the kinds of energy storage systems, lithium ion batteries are remarkable, because they show high energy density, stable discharge voltage and long shelf life [3–6]. However, lithium ion batteries also suffer from some limitations, such as its toxicity, high cost and combustible organic solvents, which may cause some safety problems especially when it is out of control such as overcharging or short-circuiting [7–9]. As a result, the drawbacks above limit their application in large-scale batteries. In 1994, Dahn et al. proposed a new type of lithium ion battery [10] with aqueous electrolytes, VO_2 anode and LiMn_2O_4 cathode (denoted as $\text{VO}_2//\text{LiMn}_2\text{O}_4$). Compared with the conventional flammable electrolytes, it could operate in environmentally friendly aqueous electrolytes as well as possess highly ion conductivity. Afterwards, a large number

of aqueous lithium ion batteries have been proposed such as $\text{LiV}_3\text{O}_8//\text{LiCoO}_2$ [11], $\text{LiTi}_2(\text{PO}_4)_3//\text{LiMn}_2\text{O}_4$ [12], $\text{Li}_x\text{V}_2\text{O}_5\text{-PPy}//\text{LiMn}_2\text{O}_4$ [13], $\text{PPy}//\text{LiCoO}_2$ [14] and $\text{Zn}//\text{LiMnPO}_4$ [15].

Recently, Yan et al. have proposed a novel rechargeable hybrid aqueous battery system [16] using two weak acidic electrolytes (Li^+ and Zn^{2+} of chloride salt in aqueous solution). The function mechanism is that Li^+ inserts into LiMn_2O_4 cathode and Zn^{2+} deposits on Zn anode at charge, then back to the solution of Li^+ and Zn^{2+} at discharge, respectively. Subsequently, similar battery systems have been reported with a longer cycling life, such as $\text{Zn}//\text{Na}_{0.95}\text{MnO}_2$ [17] and $\text{PbSO}_4//\text{LiMn}_2\text{O}_4$ [18], while the aqueous battery has a small capacity and has a low energy density in usual. In addition, $\text{Zn}//\text{Na}_{0.95}\text{MnO}_2$ has the inherent safety issue, such as dendrite formation on the Zn anode at charge, and $\text{PbSO}_4//\text{LiMn}_2\text{O}_4$ uses heavy metal of Pb. To overcome these shortages, it is necessary to improve the performance of anode materials. Zn is an attractive candidate of anode material [19] for aqueous battery because of its low equilibrium potential (-0.762 V vs. standard hydrogen electrode, SHE), abundance, low cost, low toxicity, and high specific energy.

Compared with planar Zn, porous Zn material as anode is more widely used for battery [20,21], because it possesses higher surface area and could be easy to contact to the electrolyte. High surface area makes the passivation of Zn in charge process, especially when the hydrogen evolution on Zn makes the passivation growing

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intensity [22]. In order to solve this problem, some additives are added to the porous Zn anode. In the selection of the additive material, the requirements are taken into account, such as enhancement of the network at low additive concentration, excellent inter-particle contact, electrolyte access optimization, inert materials. And then, a series of oxides are used to weaken the passivation of Zn and hydrogen gas evolution, such as HgO [23], PbO [24], CdO [25], V₂O₅ [26], B₂O₃ [27], etc. From the viewpoint of environmental protection and economic benefit, the additives above can not meet the requirements. So it is still urgent to develop some novel and efficient additive materials. Carbon materials are applied widely in lithium ion battery, fuel cell and chemical sensor for its advantages such as high conductivity, high chemical stability, low price, non-toxicity, etc. For example, M. N. Masri et al. investigate [28] the addition of carbon black into the porous Zn anode in a Zn-air battery and the electrochemical performance is improved significantly. In this work, acetylene black (AB), carbon nanotube (CNT) and active carbon (AC) added to the porous Zn anode is investigated, respectively. Then the behaviors of the rechargeable hybrid aqueous battery (Zn//LiMn₂O₄) are studied by electrochemical method, scanning electron microscopy, and X-ray Diffraction.

2. Experimental

2.1. Preparation of anode and rechargeable hybrid aqueous battery fabrication

Zn anode slurry are prepared by mixing 80 wt% Zn powder (99.99%, Aldrich), 10 wt% carbon material (AB, CNT and AC, respectively), and 10 wt% Polyvinylidene Fluoride (PVDF) binder blending in N-methyl-2-pyrrolidone (NMP). Then the slurry is coated on a black paper current collector (surface is 1.5 cm²) and dried in a vacuum at 60 °C for 5 h. The cathode is prepared by the same method as that of the anode described above. The cathode consists of 80 wt% LiMn₂O₄, 10 wt% acetylene black, and 10 wt% PVDF. The LiMn₂O₄ is synthesized by the similar method according to our previous work. At first, MnCO₃ is first prepared by a facile hydrothermal reaction from an aqueous solution of KMnO₄ and glucose in a molar ratio of 10:1 at 180 °C. Then, the prepared oval MnCO₃ precursor is mixed with Li₂CO₃ in acetic acid under ultrasonic for 30 min. The mixture is vacuum-dried at 90 °C. Then the mixture is heat-treated at 300 °C for 3 h and 750 °C for 4 h to get LiMn₂O₄, respectively. The electrolyte is prepared by dissolving 0.5 mol L⁻¹ Li₂SO₄ and 1 mol L⁻¹ ZnSO₄ in deionized water. All of the segments are assembled to fabricate a rechargeable hybrid aqueous battery.

2.2. Electrochemical characterizations

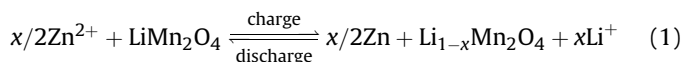
Cyclic voltammetry (CV) is carried out on a CHI 660C electrochemical workstation (Shanghai, China) with a three-electrode-cell at a scan rate of 1 mV s⁻¹ in the potential range of -0.2–2.2 V (vs. Zn²⁺/Zn). A LiMn₂O₄ and Zn is used as the working electrode, respectively, and each electrode is about 1 mg with an active area of 0.8 cm². A platinum wire is used as the counter electrode, and a Zn foil is used as the reference electrode. The galvanostatic charge–discharge tests are characterized on a battery test system TC5.X (Neware, China) at room temperature. Tafel polarization measurements are performed on the CHI 660C electrochemical system. A three-electrode cell includes a saturated calomel electrode (SCE) reference electrode, a platinum counter electrode and a porous Zn working electrode. Tafel polarization is recorded from -0.90 V to -1.25 V in 0.5 mol L⁻¹ Li₂SO₄ and 1 mol L⁻¹ ZnSO₄ aqueous electrolyte at the scan rate of 0.5 mV s⁻¹.

2.3. Physical characterizations

The morphologies and structures of the prepared Zn anode are characterized by scanning electron microscopy (SEM, Hitachi S-4800, 25 kV) and X-ray diffraction (XRD, Shimadzu 6000, Ni-filtered Cu K_α radiation).

3. Results and discussion

CVs of Zn and LiMn₂O₄ electrodes in 0.5 mol L⁻¹ Li₂SO₄ and 1 mol L⁻¹ ZnSO₄ aqueous electrolyte at the scan rate of 1 mV s⁻¹ are shown in Fig. 1. In the case of Zn, there is one couple of clear redox peaks located at -0.20/0.15 V (vs. Zn²⁺/Zn), which are due to the reversible dissolution and the plating of Zn. In the case of LiMn₂O₄, there are two couples of reversible redox peaks at 1.70/1.75 V and 1.80/1.91 V (vs. Zn²⁺/Zn), respectively, which attribute to the two-step lithium intercalation/extraction of LiMn₂O₄ in the aqueous electrolyte. Since there is a potential difference between Zn and LiMn₂O₄ in 0.5 mol L⁻¹ Li₂SO₄ and 1 mol L⁻¹ ZnSO₄ aqueous electrolyte, they can be assembled into a battery. The system is schematically shown in Scheme 1. The proposed cathodic and anodic reactions can be described as follows:



The performance of the rechargeable hybrid aqueous batteries with pure porous Zn, Zn/CNT, Zn/AC and Zn/AB electrode are shown in Fig. 2, respectively. Fig. 2A presents the typical discharge characteristics of the batteries at the first cycle. The discharge plateau voltage is ca. 1.8 V, which is consistent with the CV data in Fig. 1. This is due to the intercalation of Li⁺ ions into the host. The initial discharge capacity of pure Zn electrode is 114 mAh g⁻¹. When acetylene black, carbon nanotube and active carbon is added to the pure Zn anode system, the discharge capacity increases to 130, 140 and 150 mAh g⁻¹, respectively. It suggests that the introduction of carbon material in the porous Zn anode improves the discharge capacity. Among them, active carbon is the best one due to its highest specific surface area that provides more sufficient reaction channels.

Fig. 2B shows the cycling characteristics of the pure porous Zn, Zn/CNT, Zn/AC and Zn/AB anode at the current density of

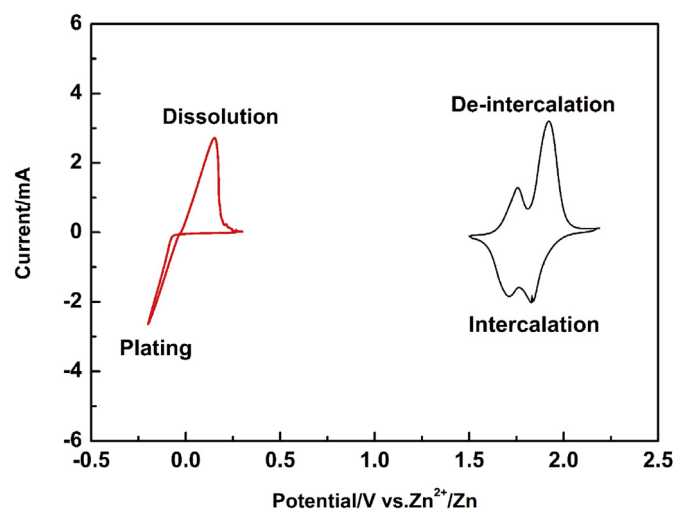


Fig. 1. CVs of Zn and LiMn₂O₄ in the aqueous electrolyte of 0.5 mol L⁻¹ Li₂SO₄ and 1 mol L⁻¹ ZnSO₄ at the scan rate of 1 mV s⁻¹, which is tested by using platinum and Zn as the counter and reference electrode, respectively.

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