



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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



Influence of different silica gelling agents on the performance of aqueous gel electrolytes

Changyu Lu^{a,b,1}, Tuan K.A. Hoang^{b,1}, The Nam Long Doan^{b,1}, Matthew Acton^b, Hongbin Zhao^{b,c}, Weisheng Guan^a, P. Chen^{b,*}

^aSchool of Environmental Science and Engineering, Chang'an University, Xi'an, 710054, PR China

^bDepartment of Chemical Engineering and Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L3G1, Canada

^cDepartment of Chemistry, College of Science, Shanghai University, Shanghai, 200444, PR China

ARTICLE INFO

Article history:

Received 4 June 2016

Received in revised form 15 July 2016

Accepted 23 July 2016

Available online xxx

Keywords:

Rechargeable battery

Aqueous electrolyte

Gel electrolyte

Amorphous silica.

ABSTRACT

In this study, gel electrolytes are prepared from silica gelling agents and aqueous electrolyte for application in the rechargeable hybrid aqueous battery for the first time. The required quantities of silica materials are in the range of 4–15 wt.%. The gelling time is in the magnitude of minutes and the ionic conductivities of gel electrolytes are in the range of 50.6–60.6 mS cm⁻¹. These batteries using these gel electrolytes exhibit higher rate capability, slower self-discharge (ca.15% after 24 h), and up to 10–12% higher cyclability compared with the performance of the batteries using the conventional liquid electrolyte.

© 2016 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

Introduction

One of the first prototypes of lithium-ion batteries using aqueous-based electrolyte was introduced in 1994 [1]. Up to date, cathode and anode developments of the rechargeable aqueous lithium ion batteries (ARLBs) have attracted research interests [2–6]. However, the electrolyte and the separator are important parts of the batteries and recent work regarding the elimination of oxygen in the electrolyte leads to enhancement in cycling stability [7]. We propose improvement of the ARLBs further by design and development of aqueous gel electrolytes. This is because gel electrolytes offer multiple advantages to batteries [8]. When using gel electrolytes in Li-ion batteries, dendrite formation on the anode is suppressed, the endurance to varying electrode volume during cycling is enhanced, the reactivity between the anode and the liquid electrolyte is reduced, safety is improved, and better shape flexibility and manufacturing integrity are achieved. According to Walls et al. [9], non-aqueous polymer electrolytes of LiBs have been developed by adding different forms of silica in the

electrolytes. Upon the addition of silica into the electrolyte, the electrolyte–electrode interfacial resistance decreases. The growth of lithium dendrites on the surface of lithium metal anodes can be suppressed [10]. The thermal-deformation of gel polymer electrolyte is diminished up on addition of silica filler [11].

Recently, there are new emerging types of batteries, which use two types of cations in the electrolytes. For example, the rechargeable hybrid aqueous batteries use Zn²⁺ and Li⁺, where the anode is a first order electrode made by Zn and the cathode is a lithium intercalation material [12]. It is worth noted that the LiMn₂O₄ material is an excellent cathode material in both aqueous and non-aqueous batteries [13,14]. This material has been exploited in different morphologies, including nanochains [15], nanorods [16], and nanotubes [17]. Work regarding the aqueous Mg batteries which use Mg²⁺, Li⁺ in the electrolyte has been reported [18]. However, there is no recent work about aqueous gel electrolyte except several typical publications focused on the gelled electrolyte of a Zn-air battery [19].

Current research in our laboratories focuses on the development of new gel electrolytes for use in the rechargeable hybrid aqueous gel batteries in order to reach commercialization. Toward this trend, we have proved that the batteries use silica nanoparticle doped electrolytes can perform better than batteries using conventional liquid electrolytes [20]. The rate capability and the

* Corresponding author. Tel.: +1 519 888 4567x35586; fax: +1 519 888 4347.

E-mail address: p4chen@uwaterloo.ca (P. Chen).

¹ These authors contributed equally.**

cyclability increased, the float charge current decreased and the open circuit voltage drop decreased [20].

In this work, five types of silica materials are used to prepare gel electrolytes. These materials are less expensive and commercially available in large quantities. Furthermore, they are previously used in the formulation of gel electrolytes in lithium-ion batteries and lead-acid batteries [8–12,21]. Pre-optimization was conducted so that usage of each type of silica is at the minimum requirement for gel preparation. Effects of different types of silica toward the performance of the rechargeable hybrid aqueous gel batteries are presented.

Experimental

Preparation of batteries

Preparation of anode and cathode: the electrodes are prepared following previously described procedures [12,20].

Preparation of electrolyte: The electrolyte was prepared by adding 130.57 g of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (Sigma Aldrich, 98%) and 146.20 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma Aldrich, 98%) in deionized water and adjusted to 500 mL. It contains 2 M Li_2SO_4 and 1 M ZnSO_4 , pH was adjusted to 4.00 ± 0.05 by a few drops of concentrated LiOH or H_2SO_4 aqueous solution. Batteries prepared from this electrolyte is named the “conventional”. Gel electrolytes containing 5 wt.% Fumed Silica (Sigma Aldrich), 12 wt.% Nano-Silica (Sigma Aldrich), 15 wt.% Shandong Fumed Silica (Shandong Zhonghai New Material Group, China), 4 wt.% Dingxiang Fumed Silica (Shandong Dingxiang Technology Co. Ltd., China) and 4 wt.% Xiangrun Silica Aerogel (Shandong Zhonghai New Material Group, China) were prepared by mixing the respective silica powder with the conventional liquid electrolyte. Batteries prepared from such electrolytes will be named as “Sil1”, “Sil2”, “Sil3”, “Sil4” and “Sil5”, respectively. The silica quantities were previously optimized so that each type of silica is used at minimum quantity required for gelling.

Physical characterization

Surface area and porosity of the silica powders were characterized by the accelerated surface area and porosimetry analyzer (ASAP2020, Micromeritics) using a 20-points nitrogen adsorption and desorption program. Functional groups of different silica and their corresponded gel electrolytes were analyzed by Fourier Transform Infrared Spectroscopy (FT-IR, Brüker). Fresh cathode and anode, post-battery-run cathodes and anodes are examined by powder X-ray diffraction (XRD, D8 Discover, Brüker) instrument equipped with $\text{Cu-K}\alpha$ radiation source, with a scan speed of 1° per minute, ranging from 10° to 90° .

Electrochemical characterizations

The ionic conductivity of the pristine aqueous electrolyte and the gel electrolytes were measured on an Orion 4-Star pH-Conductivity meter, equipped with an Orion 013605MD conductivity probe. The electrochemical tests were investigated via Swagelok-type cells. Each cell was composed of a positive electrode and a polished zinc metal negative electrode, separated by an Absorbent Glass Mat (AGM) separator. The composite cathode consists of 86 wt.% of LiMn_2O_4 (MTI), 7 wt.% of carbon KS-6 (Timcal), and 7 wt.% of polyvinylidene fluoride (Kynar[®] HSV 900) as the binder. Aqueous electrolyte was dropped onto the AGM separator and gel electrolytes were injected into the separator (ca. 0.40 g) by using a syringe. Fresh gel electrolytes could be soaked into the separator in a vacuum chamber when the gels were still liquid. Cyclic voltammetry (CV) tests were conducted on a multi-channel potentiostat (VMP3, Biologic) between 1.4 and 2.1 V vs.

$\text{Zn}^{2+}/\text{Zn}^\circ$ at a scan rate of 0.1 mV s^{-1} . In addition, AC impedance measurements were performed with amplitude of 10 mV at the applied frequency range from 0.1 Hz to 1 MHz. The various charge–discharge performances were tested on a multi-channel battery tester (BTS-5V5mA and BTS-5V10mA, Neware) between the voltage of 1.4 and 2.1 V vs. Zn^{2+}/Zn (1 C is defined as 115 mA g^{-1}). All electrochemical data were obtained at room temperature.

Results and discussion

Fig. 1 represents the adsorption and desorption isotherms of five different silica types. The adsorption–desorption behaviors of all silica materials are reversible without recognizable hysteresis. Thus, they can be classified as Type-II isotherms even though several silica types possess inner micro-porosity [22]. The adsorption data and the specific quantity required to prepare gel electrolytes are presented on Table 1. For example, if Sil1 is used, one needs to mix 5 wt.% of this silica with 95 wt.% of the conventional aqueous electrolyte so that the gel electrolyte can be obtained. The required quantity for gelling is varied among silica materials. Sil3 has very high surface area, up to $658.53 \text{ m}^2 \text{ g}^{-1}$, however, one needs up to 15 wt.% of this silica for gelling with aqueous electrolyte. This quantity is too high since the required quantities of silica for gelling in lead-acid batteries are in the range of 6.0–12 wt.% [23,24]. It is worth noted that the non-porous silica requires higher quantity for gelling (7.0–11.5 wt.%) while porous fumed silica can be used as smaller concentration (6.0 wt.%). In this case, the internal surface area and the pore volume may be more important factors. Required quantity of Sil3 is the highest may be due to its lowest pore area and lowest pore volume. Sil2 Exhibits $0.38 \text{ cm}^3 \text{ g}^{-1}$ of pore volume so that the required quantity for gelling is slightly smaller than that of Sil3. One needs 12.0 wt.% of Sil2 to be able to prepare gel with liquid electrolyte. Sil1, Sil3, and Sil4 possess high pore volume of 0.63 – $0.74 \text{ cm}^3 \text{ g}^{-1}$ and these silica only requires 4–5 wt.% for gelling. It is concluded that the internal surface area and the pore volume are more important factors to consider when evaluating a silica for gelling purpose. This also suggests that the liquid electrolyte tends to be drawn in the porous space due to the capillary force at the pore slit or pore opening. These forces abstract the liquid inside the void space of the silica materials.

Silica materials possessing higher pore volumes also provide shorter gelling time (Table 2). Gel prepared from 15 wt.% of Sil3 and 85 wt.% of conventional liquid electrolytes requires up to 17 h

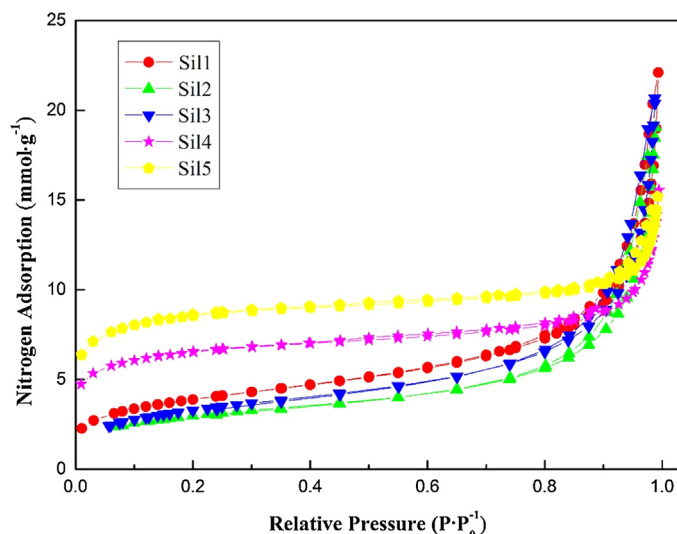


Fig. 1. Nitrogen adsorption and desorption isotherms of the silica materials.

Download English Version:

<https://daneshyari.com/en/article/6669412>

Download Persian Version:

<https://daneshyari.com/article/6669412>

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