



# Rechargeable hybrid aqueous batteries using silica nanoparticle doped aqueous electrolytes



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## HIGHLIGHTS

- The first use of silica nanoparticle doped electrolyte has been demonstrated.
- Enhancement of open-circuit voltage is observed when batteries are under storage.
- Decrease in back-current is observed when batteries are under constant charging.
- Enhancement of rate capability and cycle life are observed.

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## ABSTRACT

Silica nanoparticles doped aqueous electrolytes have been prepared and implemented for the first time in rechargeable hybrid aqueous battery systems (ReHABs). The batteries were assembled from a cathode containing  $\text{LiMn}_2\text{O}_4$  – a lithium intercalation compound, a zinc metal foil anode and a sulfate electrolyte containing  $\text{Zn}^{2+}$  and  $\text{Li}^+$  ions. Silica nanoparticles were doped into the liquid electrolyte with the initial aim to create a silica containing gel electrolyte. However, the 5% and 10%  $\text{SiO}_2$  doped electrolytes were viscous and could be easily absorbed in the Absorbed Glass Mat (AGM) separator and the whole system (doped electrolyte + AGM) immobilized after a few minutes. The AGM loaded with silica doped electrolytes remained wet after storage for weeks under ambient condition thanks to the water retention ability of nanoscale silica particles. The doped silica nanoparticles restrained deposition of zinc dendritic crystals, and reduced float charge current and self-discharge. The ReHABs assembled from the silica nanoparticles doped electrolytes provided high specific discharge capacity, up to 140 mAh  $(\text{g LiMn}_2\text{O}_4)^{-1}$  at 0.2 C, and the cyclability of such systems was significantly enhanced compared to the ReHABs assembled from conventional electrolytes. X-ray Diffraction revealed that the anode of the batteries using  $\text{SiO}_2$  doped electrolytes were protected since only the XRD peaks of Zn were detected after the batteries were running 700 cycles of charge and discharge.

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## 1. Introduction

Recently, energy shortage and environment pollution have become serious issues due to the economic development and the population increase [1]. Renewable energy sources such as solar [2] and wind energy [3] have been developed rapidly. These require low cost, safe, and environmentally friendly energy storage systems [4,5]. Large scale batteries or battery-stacks are great

candidates. Comparing with the traditional batteries, such as lead-acid, nickel–cadmium (Ni–Cd), nickel–metal hydride (Ni–MH) and redox flow-cells (RFCs), lithium-ion battery system (LiB) has been demonstrated to be one of the most promising stationary power sources with high-energy, high-power density, long lifetime and light weight [6–9]. Therefore, LiBs have attracted the attention of scientists and have been studied widely. However, despite their remarkable performance, LiBs employ highly toxic and flammable organic solvents in the preparation of electrolytes and this causes safety hazards if used improperly. In addition, manufacture procedures of LiBs are complicated and expensive, partly because the electrolytes are sensitive to moisture and air. These challenging

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issues hinder the application of LiBs in the large-scale energy storage systems [10].

In 1994, Dahn's group [11] reported a new type of rechargeable lithium-ion battery using aqueous based electrolytes as replacements of organic based electrolytes. The newly developed system is namely the aqueous rechargeable lithium-ion batteries (ARLBs). Beside the safety improvement, ionic conductivities of aqueous based electrolytes are larger than their organic analogs by several orders of magnitudes.

The first prototypes of ARLBs suffered from poor cycling performance. Nevertheless, they attracted more attention of researchers to improve this aqueous system still further. In ARLBs, both cathode and anode are lithium intercalation compounds and the electrolyte is a lithium-containing aqueous solution. Most of the studies focus on electrode development to enhance power density, energy density, specific energy, cyclability, and safety issues [12–14]. However, as a crucial part of ARLBs, properties of electrolytes such as ion concentrations, pH, dissolved oxygen concentration, ionic conductivities and additives are important factors that affect the electrochemical performance. Recently, rechargeable hybrid aqueous batteries (ReHABs) have been introduced [15,16]. ReHABs use  $\text{LiMn}_2\text{O}_4$  in the cathode, zinc foil as the anode, and an aqueous electrolyte containing  $\text{Zn}^{2+}$  and  $\text{Li}^+$  ions. There are several technical issues which must be solved to ensure the delivery of this system to the market.

First, the ReHABs are apt to occur zinc deposition of dendritic crystals in charging and discharging process for a long period along reversible redox reaction of zinc on one side of a negative electrode so as to cause piercing of a separator and efficiency loss caused by battery short circuit [17]. Second, similar to other battery systems, the ReHABs suffer from self-discharge. Self-discharge is a process that decreases capacity of the cell without flow of current through an external circuit when batteries are under storage. This capacity loss is normally accompanying with the decrease in open circuit voltage (OCV) of the cell after a long period of time [18]. On the other hand, in application such as uninterruptible power supply (UPS), batteries consume electrical power under constant charging after they have been already charged to full capacity. This is because there is a back current inside the battery, which is named the float current. In case of lead-acid batteries, if this current is too high, the cell might cause sulfation due to undercharging, lead to shorter cycle life of batteries [19]. In ReHABs, higher float charge current is related with larger volume of oxygen being generated from the decomposition of water at high working potential. Thus, minimization of the float current is one of the main tasks and many researchers have been trying to use coating materials to protect the surface of electrodes or add soluble additives in the electrolytes [20,21]. Last but not least, the poor water retention ability of ReHABs leads to pH and concentration change in the electrolyte which results in rapidly declining of the battery capacity. The move from pristine aqueous electrolytes to silica nanoparticles doped electrolyte is logical because doped silica protect water in the electrolyte from evaporation and thus retain the stability of the battery system.

Silica nanoparticles have been used in gel electrolytes of lead-acid [22] and gel polymer electrolytes of LIBs due to its good thixotropy and reliability under cyclic or deep-discharge conditions [23]. In this work, liquid electrolytes doped with silica nanoparticles have been prepared and implemented first time in ReHABs. Silica nanoparticles were doped into the electrolyte with an aim to reduce the drop of open-circuit potential and reduce the self-discharge rate. When using silica doped electrolyte in ReHABs, higher specific discharge capacity, lower self-discharge rate, lower float charge current density, higher rate capability and better cyclability have been demonstrated. Moreover, the silica nanoparticle doped electrolyte enables ReHABs to obtain even and smooth zinc deposition, effectively avoids production of the dendritic crystals, and thus greatly reduces probability of battery short circuit.

## 2. Experimental

### 2.1. Battery preparation

Preparation of cathode:  $\text{LiMn}_2\text{O}_4$  (MTI Co.), KS-6 (Timcal), and polyvinylidene fluoride (PVdF, Kynar) (86:7:7 wt.%) in *n*-methyl-2-pyrrolidinone (NMP, Sigma Aldrich Co.) were mixed thoroughly, and then casted on graphite foil (Alfa Aesar). After vacuum drying at 60 °C for 6 h, they were cut by disks of 12 mm diameter (typical active material load of 5–6 mg  $\text{cm}^{-2}$ ) and soaked in the electrolyte solution under reduced pressure before battery assembly.

Preparation of anode: the anode was prepared from zinc foil (Rotometals, 99.6% purity). The 0.3  $\mu\text{m}$  polishing powder (Boehler) dispersed in de-ionized water and a nano-cloth (Boehler) were used to polish the zinc foil. After that, it was washed with soap and deionized water, followed by rinsing with anhydrous ethanol and drying at 60 °C under vacuum for 30 min; the dried-zinc was cut by rounded disks of 12 mm diameter and stored in anhydrous ethanol solution before battery assembly.

Preparation of electrolyte: 129.25 g of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (Sigma Aldrich, 99%) and 145.23 g of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (Sigma Aldrich, 99%) were stirred vigorously for 24 h in 250 mL of deionized water until all salts were dissolved. Then, the volume of obtained solution was adjusted to 500 mL and pH was adjusted to  $4.00 \pm 0.05$  by a few drops of concentrated LiOH aqueous solution. The obtained electrolyte contains 2 M  $\text{Li}_2\text{SO}_4$  and 1 M  $\text{ZnSO}_4$ . Batteries prepared from this electrolyte is named the “conventional”. Metastable suspension electrolytes containing 5 wt%  $\text{SiO}_2$  and 10 wt%  $\text{SiO}_2$  were prepared by mixing conventional liquid electrolyte with as-received silica nanoparticles (Sigma Aldrich) so that the final weight percent of  $\text{SiO}_2$  reach predetermined values. Batteries prepared from such electrolytes will be named as the “5%  $\text{SiO}_2$ ” and the “10%  $\text{SiO}_2$ ”, respectively.

### 2.2. Physical characterizations

Silica nanoparticles were characterized by the accelerated surface area and porosimetry analyzer (ASAP2020, Micromeritics) using a 20-points nitrogen adsorption and desorption program, and by powder X-ray diffraction (XRD, D8 Discover, Bruker) technique equipped with  $\text{Cu K}\alpha$  radiation, with a scan speed of 1° per minute, ranging from 10° to 100°. Fresh cathode and anode, post-battery-run cathodes and anodes are characterized by XRD and field emission scanning electron microscopy (FE-SEM, Leo-1550, Zeiss) using extra high tension (EHT) of 8 kV.

The state of electrolyte in AGM separator was visualized by mean of microscope. First, the separator was loaded with electrolyte until it was fully wet. Then, the wet separator was manually cut into thin pieces with thickness of ca. 0.5 mm. The thin pieces were placed in petri dish (Fisher Scientific) so that the light source of the microscope can be transmitted from intersection to intersection on a microscope EVOS FL cell imaging system (Life Technology), with a 40× objective lens. Images were captured as monochrome, with Sony ICX445 CCD of 1.3 megapixels installed on the microscope.

Thermo-gravimetric analysis (TA Instrument Q-600) was conducted from 20 °C to 120 °C (1 °C  $\times$  min<sup>-1</sup>) to determine the thermal stability of electrolytes in AGM. All measurements were performed in triplicate.

### 2.3. Electrochemical characterizations

The ionic conductivity of the pristine aqueous electrolyte and the gel electrolytes was conducted on an Orion 4-Star pH-Conductivity meter, equipped with an Orion 013605MD conductivity probe. Measurements were conducted in triplicate. Electrochemical perfor-

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