



Synthesis of porous magnesia fibers with enhanced performance as a binder for molten electrolyte



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ABSTRACT

This paper describes the synthesis and properties of the porous MgO fibers used as a binder of the electrolyte for thermal batteries. Porous MgO fibers with controlled pore size were prepared by a facile hydrothermal method in the presence of polyethylene glycol (PEG). The effect of PEG addition on the pore sizes of the porous MgO fibers was systematically investigated. The influence of porous MgO fibers having different pore sizes on the electrolyte (LiCl–KCl) leakage and electrochemical performances of the corresponding model cells were measured. The results show that a large amount of PEG leads to porous MgO fibers having high specific surface area and total pore volume, and reaching the maximum, $13.65 \text{ m}^2 \text{ g}^{-1}$ and $0.097 \text{ m}^3 \text{ g}^{-1}$ respectively, at 1.5 mol% of PEG addition. The model cell fabricated with porous MgO fiber having high surface area and pore volume shows low deformation and electrolyte leakage, as well as high discharge capacity. Electrochemical impedance spectroscopy (EIS) analysis shows that, the ionic conductivity of the cell increases as the porous MgO fiber pore size increasing. These performances are much better than the performances of cell fabricated with traditional MgO powders. The dimensional stability and large surface area contact of porous MgO fibers with molten electrolyte should account for the superior physical and electrochemical performances of model cell fabricated with porous MgO fibers.

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1. Introduction

Thermal battery is a kind of primary battery working at 450–550 °C utilizing molten salts as electrolyte, which possesses high power density, reliability and long storage capabilities [1,2]. It is widely applied in military weapons [3] as activating power source. However, in order to prevent the leakage of molten electrolyte and, in consequence, shortage of the electrodes, the electrolyte is usually immobilized by some inert binders such as SiO_2 , TiO_2 , ZrO_2 , BN, and ceramic fibers [4–8]. The application of these materials is limited since they are costly, have poor wettability with electrolyte and react with electrodes [6,8]. Until now, MgO powders have been used as the most efficient and useful binder due to its low cost and superior physical and chemical stability [9,10]. And the MgO powders prepared by thermal decomposition of magnesium hydroxide or magnesium carbonate hydroxide [10] are widely employed to immobilize the molten electrolyte in thermal batteries, at about 35–50 wt.% concentrations [11–15]. Czajka

et al. [16] reported that MgO powders modified by MgF_2 show good immobilizing effect, but have very low ionic conductivity in the range of $0.02\text{--}0.04 \text{ S cm}^{-1}$. Cheong et al. [17] reported that ceramic fibers having net structure show good dimensional stability when they are used as binder and the corresponding electrolyte pellets also show well electrochemical performance, but the ceramic fibers have poor wettability to molten electrolyte.

Up to now, a binder that can enhance the immobilizing effect and does not reduce ionic conductivity is seriously required. In our previous works [18,19], we have developed MgO fibers and porous MgO fibers as binder for molten electrolyte. The obtained results show that fibrous and porous structure of the MgO fibers can result in large network structure, and thus a strong adsorption capacity to molten electrolyte, finally significantly enhanced immobilizing effect were obtained compared with traditional MgO powders. Moreover, pore size distributions in porous MgO fibers are very important to the performances of corresponding model cell. That is because pore size distributions directly affect specific surface area and network structure for molten electrolyte adsorption and ionic migration channels in thermal battery. So, the preparation of porous MgO fibers with controlled pore size is of greatest importance, nevertheless, there are few reports about it. However,

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Jo et al. [20] reported a synthesis of porous TiO_2 particles through hydrothermal method in the presence of PEG; while Yan et al. [21] prepared 1D MgO by calcining magnesium hydroxide sulfate (MHSH). In our work, we learn from the two methods and obtain a new way to prepare porous MgO fibers with controlled pore sizes.

Therefore, we further explore the influences of pore size distributions of porous MgO fibers on the properties of electrolyte pellets and the performance of the corresponding model cell. The aim of this work is to prepare porous MgO fibers with controlled pore size and distribution via a hydrothermal method and use the prepared porous MgO fibers as a binder for the molten electrolyte (KCl–LiCl). Moreover, the influences of pore size distributions of the porous MgO fibers on the electrolyte leakage and ionic conductivity of the electrolyte-binder pellets and the discharge capacity of corresponding model cell were investigated.

2. Experimental

2.1. Synthesis of porous MgO fibers

Porous MgO fibers were prepared from calcining magnesium hydroxide sulfate hydrate (MHSH) fibers which were synthesized via a hydrothermal method in the presence of PEG. All the reagents ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and NaOH, AR) in the current experiments were used as received without further treatment. Ultrapure water with resistivity of $18.25 \text{ M}\Omega \text{ cm}$ was used as the solvent. Firstly, NaOH solution (20 mL, 3 M) was gradually dropped into stirring MgSO_4 solution (60 mL, 2 M) containing different amount of PEG ($n(\text{PEG})/n(\text{MgSO}_4) = 0, 0.5 \text{ mol}\%, 1.0 \text{ mol}\%, 1.5 \text{ mol}\%$ and $2.0 \text{ mol}\%$) at room temperature. Secondly, the mixed solution continued to stir for 1 h, followed by transferring into 100 mL Teflon-lined autoclave and then kept in an oven at 160°C for 15 h. After the reaction, MHSH precursors were obtained, washed by ultrapure water and dried at 80°C in air. Finally, the precursors were calcined at 1000°C for 4 h to produce porous MgO fibers.

2.2. Preparation of electrolyte binder pellets

A eutectic mixture of 44.8 wt.% LiCl and 55.2 wt.% KCl (sieved to 200 mesh) with a melting temperature of 352°C was used as the electrolyte [1,16]. Initially, the prepared electrolyte was dried at 250°C for 24 h. Electrolyte binder (EB) pellets were prepared by mixing the dried electrolyte and the prepared MgO fibers using liquid nitrogen mixing method [15], and melted at 500°C for 8 h [9]. Then, the obtained uniform mixtures containing porous MgO fibers with different pore sizes and distributions were compacted into disk-shaped pellets with a diameter of 2.2 cm and a thickness of about 3 mm at a static pressure of 4 MPa in a dry room. For comparison, parallel pellets were made by the same method using traditional MgO powders which were obtained by calcining magnesium hydroxide at 1000°C as binder.

2.3. Characterization

The thermal analysis of the MHSH precursors was studied in the temperature range of $30\text{--}1000^\circ\text{C}$ with a heating rate of $10^\circ\text{C min}^{-1}$ at air atmosphere, using the differential thermo analyzer (TGA, SDT Q600, Setaram) equipped with a TG measurement unit. The morphologies of the materials (porous MgO fibers and EB powder) were investigated using field emission scanning electron microscopy (FESEM; Ultra 55, Zeiss) equipped with an energy dispersive X-ray detector (EDX). The specific surface areas of the porous fibers were measured using a nitrogen adsorption analyzer (Autosorb-1MP) with the BET equation and the pore size distributions were analyzed from the adsorption branches of the isotherms based on the Barrett-Joyner-Halenda (BJH) method.

To measure the electrolyte leakage, EB pellets were put in a crucible and covered with MgO powders, then maintained at 500°C for 30 min. The whole operation process was in a drying room with a humidity lower than 0.1 RH%. The electrolyte leakage of the EB pellets was evaluated by calculating the mass loss per unit surface area of the pellets. Meanwhile, in order to reduce the error, electrolyte leakage of the pellets was the average value of three samples with the same composition. The electrochemical impedance spectroscopy (EIS) of pellets was performed using an electrochemical workstation (CHI 760C, CH Instruments, China) in the frequency range from 100 kHz to 0.01 Hz at open circuit potential with an AC perturbation of 5 mV. The testing temperature was 450°C and the ionic conductivity could be calculated by continuously vary cell constant (CVCC) technique [22], and the equation is:

$$\sigma = \frac{1}{A \left(\frac{d(R_s + R_p)}{dL} \right)} \quad (1)$$

Where σ is the ionic conductivity, $R_s + R_p$ is the circuit resistance, L is moving distance of counter electrodes and A is the area of the SS electrode ($A = 0.2266 \text{ cm}^2$).

A model cell consisted of a cathode (0.4 g, 78 wt.% FeS_2 and 22 wt.% LiCl–KCl), an EB powder (0.3 g) and an anode (0.2 g, Li/Si alloy). The electrolyte and electrodes were alternately spread layer by layer. Graphite foil was used at the bottom and top of the cell to collect current. The cell was pressed into 17 mm diameter pellet under a static pressure of 8 MPa. The KENWOOD DDS60-6 and Agilent 6060B DC electronic load were employed to provide a constant current. Agilent 34,401 A was used to monitor potential variations between the anode and cathode of cells during the discharging process and voltage values were recorded every 0.1 s. The discharge experiments were performed at 500°C in a dry room. Three experiments were taken at each composition to ensure the reliability of the discharging data of the model cell.

3. Results and discussion

3.1. Thermal analysis of MHSH

Fig. 1 shows TG and DTA curves of the MHSH precursor. TG curve shows that significant mass loss of the MHSH precursor occurs at three distinct steps, i.e., up to 340°C , $340\text{--}750^\circ\text{C}$ and $750\text{--}1000^\circ\text{C}$, accompanying with a mass loss of 8.11%, 20.16% and 17.88% respectively. After considering the crystal structure, a three-step decomposition scheme is assumed: firstly, removing crystalline water of precursor indicating the endothermic peak at around

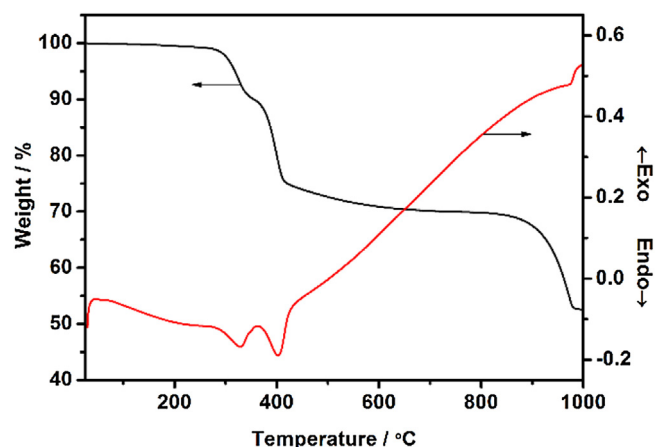


Fig. 1. TG-DTA curves of MHSH precursor.

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