



PEO/hollow mesoporous polymer spheres composites as electrolyte for all solid state lithium ion battery

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ABSTRACT

Practical, high-yield mesoporous organic polymer (MOP) spheres were successfully synthesized by a novel self-template method, which can be used as fillers to prepare poly (ethylene oxide) (PEO)-based polymer electrolytes membranes. The result shows that both the electrical conductivity and lithium-ion conductivity of PEO-based electrolytes can be improved effectively by adding the MOP filler. The electrolyte membranes are mechanically robust, thermally stable to over 270 °C, and can effectively block dendrites penetrating from metallic-lithium anode to cathode. The Li⁺ transfer conductivity of composite electrolyte membrane increases to $4.4 \times 10^{-4} \text{ S cm}^{-1}$ at 63 °C. All-solid-state LiFePO₄/MOP-PEO-LiTFSI/Li cell shows excellent cycling (144 mAh g⁻¹ after 300 cycles) and rate (167 mAh g⁻¹ at 0.2 C, 170 mAh g⁻¹ at 0.5 C, 160 mAh g⁻¹ at 1 C and 145 mAh g⁻¹ at 2 C) performance.

1. Introduction

Solid polymer electrolyte (SPE) with outstanding performances is considered as one of the ideal electrolytes for LIBs due to its excellent safety performance, good flexibility and light weight. Furthermore, the SPE can not only successfully overcome the disadvantage of traditional liquid electrolyte, such as leakage of liquid and corrosion of electrodes [1,2], but also exhibit the good flexibility and wonderful film-forming properties, which makes it possible to be applied in many occasions with the special request for the shape of cells [3,4].

However, the SPE still confronted with several problems which limit its application in lithium ion batteries, such as the weakness of lithium ion conductivities of polymers and the failure of PEO-based polymer membranes in blocking the growth of lithium dendrite across the cathode [5–7]. To overcome this problem, several methods have been attempted. Generally, it can be divided into two categories which including chemical methods and physical methods. Chemical methods such as copolymerization and cross-linking can be adopted to bring in EO bond which can incorporate with Li ion to form complex [8,9]. Physical methods such as plasticizing and blending also can improve the conductivities. The blending that mixes up the base materials with various sorts of fillers is a very important method [10–12].

Originally, it was found that some lithium salts additives in the PEO-

base can improve the Li-ion conductivity, but unfortunately it is difficult to meet the requirements of practical application [12]. Among all of the fillers, mesoporous materials take the advantages due to their potential applications in the field of energy storage [13–15]. It's worth noting that mesoporous organic polymer (MOP) built on various organic unites shows superior chemical tailorability, large surface areas, and high thermal stability owing to the unique construction [16,17].

Herein, we will first introduce a novel self-template method for the formation of MOP sphere fillers through a solution growth process. The initially formed aqueous “micelles” in the solution will play the role of self-template during the mesoporous forming process through dispersion method, which follows the principle of oil-water separation. The composite polymer electrolytes film with improved electrochemical performance can be obtained by mixing the MOP, PEO and lithium salt and then followed by vaporizing solvent. The performance of composite polymer electrolyte used in the all-solid-state electrolyte is investigated.

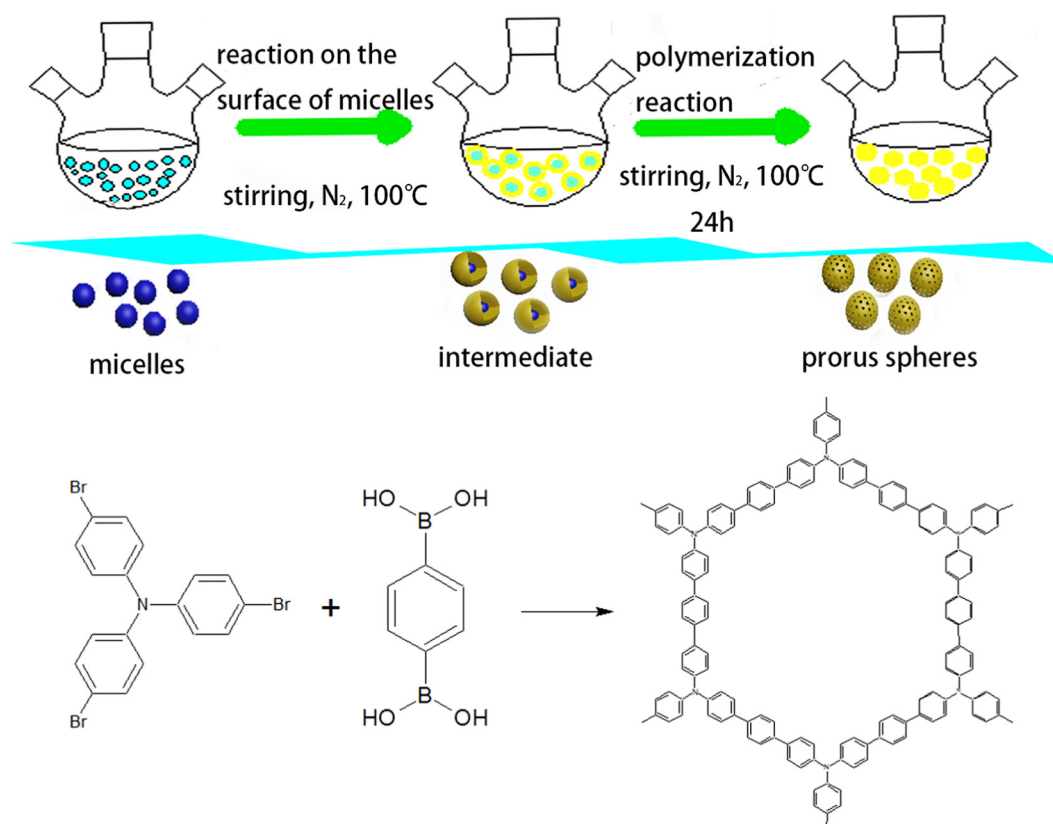
2. Experimental and characterization

2.1. Materials synthesis

The preparation for MOP is given in detail as follows. Firstly, 10 mL of 2.0 M K₂CO₃ aqueous solution was mixed with 400 mL of *N,N*-

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Scheme 1. Schematic description of the synthesis route of MOP and the reaction equation.

Dimethylformamide (DMF) solvent to form clear solution, and secondly 495 mg of 1,4-phenylenebisboronic acid and 964 mg of tris(4-bromophenyl)amine were dissolved in the above solution under continuous stirring. It should be mentioned that the tris(4-bromophenyl)amine needs to be added in three times because of the debromination reaction in the high-temperature alkaline environment. Finally, 50 mg of palladium catalyst was added and the mixture solution was stirred under nitrogen flow at 100 °C for 24 h. The product was acquired by filtering and washing with deionized water, acetone, and ethanol. The powders present slightly yellow color after further purification by Soxhlet extraction with ethanol and tetrahydrofuran for 12 h, respectively.

2.2. Preparation of MOP-PEO-LiTFSI membrane

A mixture of 300 mg MOP powders, 450 mg PEO (molecular weight $M_v = 300,000$), and 250 mg Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) was mixed and dispersed in 20 mL DMF by stirring at 60 °C to reach a certain viscosity. The mixture was poured into the polytetrafluoroethylene (PTFE) mold and dried in an oven at 65 °C to evaporate the solvent. The obtained dry MOP-PEO-LiTFSI membrane was then peeled off from the mold without cracking, cut into wafers (12 mm in diameter), and dried at 60 °C for 12 h under vacuum oven before using to assemble the coin cells.

2.3. Characterization methods

The morphologies of the as-prepared MOP powder and membranes were characterized by field emission scanning electron microscope (FE-SEM) (Zeiss Supra 40VP) and transmission electron microscope (TEM) (JEOL JEM-2100, operated at 200 kV). Brunauer-Emmett-Teller (BET)-surface area and Barrett-Joyner-Halenda (BJH) pore size distribution were measured by N_2 adsorption at liquid nitrogen temperature using a NOVA4000 automated gas sorption system. X-ray diffraction (XRD)

(Bruker D8-Advance diffractometer) was used to determine the phase of the membranes. The Fourier-transform infrared spectroscopy (FTIR) spectra were used to detect the functional groups of the MOP by using Nicolet Magna 750 IR FT-IR Spectrometer in the wave number region of 4000 to 700 cm^{-1} with 64 scans at 8 cm^{-1} resolution. Thermogravimetry (TG) (Seiko TG/DTA 7300, Japan) was used to determine the thermal stability of the composites.

2.4. Electrochemical measurements

The cathodes were prepared by mixing the active material $LiFePO_4$, carbon black, PEO and LiTFSI (60:10:20:10 by weight) in a mortar, and then the mixture was dispersed in DMF and stirred for 12 h. The obtained slurry was spread on the aluminum foil to produce cathode electrode films, which were dried at 80 °C for 12 h in vacuum oven before fabricating the coin cells in an argon-filled glove box with lithium foil as the anode and the MOP-PEO-LiTFSI membrane as the electrolyte. The assembled cells were charged and discharged at different current densities between 2.6 and 3.9 V at 63 °C on a Land 2001A Battery Testing system. The cyclic voltammograms (CV) were obtained by charging/discharging the cells on an electrochemical workstation (CHI660C, Shanghai Chenhua) at a scan rate of 0.1 mV/s. The electrochemical impedance spectrum (EIS) was recorded over the frequency range from 100 kHz to 0.01 Hz. The ionic conductivity of the electrolytes from 30 °C – 80 °C were tested by use of impedance analyzer (Biologic SP-300, France).

3. Results and discussion

Scheme 1 shows the solution-growth pathway and reaction classification for the formation of MOP powder. This chemical reaction type belongs to SUZUKI, and the quality product depends on the ratio of reactants. The solubility of products will gradually get worse with the

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