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Understanding glass fiber membrane used as a novel separator for lithium–sulfur batteries

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ABSTRACT

Glass fiber (GF) membrane is evaluated as a potential separator for lithium–sulfur batteries. It is found that GF membrane has a highly porous structure with superior thermal stability, resulting in high liquid electrolyte uptake and enhanced electrochemical performance. Li–S cells using GF membrane as the separator can retain a capacity of 617 mA h g^{-1} after 100 cycles at a current density of 0.2 C, which is 42% higher than that of cells using commercial microporous polypropylene separator. During rate capability tests, the capacity of Li–S cells using GF membrane decreases slowly from the reversible capacity of 616 mA h g^{-1} at 0.2 C to 505, 394 and 262 mA h g^{-1} at 0.5 C, 1 C, and 2 C, respectively. It should be noted that these cells can still deliver a high capacity of 587 mA h g^{-1} with a high retention of 95% when the current density is lowered back to 0.2 C. The improved cycling and rate performance are ascribed to the fact that the highly porous GF membrane can increase the intake of soluble polysulfide intermediates and slow down their rapid diffusion to the Li anode side, which can not only improve the utilization of active material, but help protect the Li anode surface as well.

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1. Introduction

Demand is increasing for rechargeable lithium batteries with higher energy density and longer cycle life since they are widely used in portable electronic devices, electric vehicles, etc. [1–12]. Sulfur (S) is considered to be one of the most promising candidates in this regard because it has the advantages of high theoretical capacity (1675 mA h g^{-1}), low cost, and environmental friendliness. However, the practical application of Li–S batteries is hindered by the low utilization of the active material, severe capacity fading, and low Coulombic efficiency.

Many efforts have been made to overcome the challenges faced by Li–S batteries. The main approaches focus on design various nanomaterials as conductive frameworks for sulfur cathodes to achieve high capacity and improve cycle life [13–19]. The active material utilization and cyclability can be improved because these conductive frameworks can enhance the electrical conductivity of the cathodes and minimize the loss of soluble polysulphide intermediates during cycling. However, those methods always involve complicated, multi-step synthetic processes, which limit their application in practical Li–S batteries.

Compared with the intensive studies on the electrode material designs, there are only few researchers working on Li–S battery separators, which are considered as a critical component in the battery system. It is well known that separators play a key role in all batteries since their main function is to keep the positive and negative electrodes apart to prevent electrical short circuit and meanwhile allow the rapid transport of ionic charge carriers that are needed to complete the path during the passage of current in an electrochemical cell [20–22]. There are many property requirements for separators used in batteries: high electronic insulation, excellent chemical resistance, good wettability with electrolyte, etc. [23–25]. Microporous polyolefin membranes are currently the most commonly-used separators for lithium batteries since they have good chemical stability and mechanical strength, but they suffer from low porosity and poor wettability with liquid electrolyte which increase the cell resistance, resulting in poor kinetics and low rate capability of the batteries. In addition, polyolefin-based separators exhibit large thermal shrinkage at high temperatures which may cause internal short circuits, fire and even explosions in case of overcharge or overheating [26].

Glass fiber (GF) membrane has received attention because it has highly porous structure and excellent wettability, which could lead to large electrolyte intake and consequently high ionic

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conductivity when placed in the electrolyte, facilitating rapid ionic transportation [27]. For example, Luo et al. introduced a glass fiber fabric separator into Li-ion batteries and achieved a capacity retention of 60% for more than 100 cycles at a current density of 40 mA h g^{-1} [28]. Zhu et al. used polyvinylidene fluoride (PVDF) coated GF as the separator for Li-ion batteries [29]. They found that a reversible capacity of 125 mA h g^{-1} could be achieved for the $LiFePO_4$ electrode at 0.2 C when the PVDF-coated GF separator was used. Recently, a hybrid separator composed of GF membrane and Celgard microporous polypropylene (PP) membrane was developed for Li–S batteries by Wang et al. [30]. Their results showed that the cell with this hybrid separator delivered a specific capacity of 1050 mA h g^{-1} at the 10th cycle with a current density of 0.2 C, which was significantly higher than that (450 mA h g^{-1}) achieved by the cell with PP membrane. However, they did not report any result on the use of GF membrane directly as the separator in Li–S batteries. In our study, we directly used the GF membrane (without the introduction of PP) as the separator for Li–S cells since the excess weight from the microporous PP membrane can decrease the gravimetric energy density as well as the volumetric energy density of the cells. In addition, the extra PP membrane can also increase the resistance of the cell and negatively affect the ionic transportation, resulting in reduced electrochemical kinetics, especially at high current densities. Experimental results showed that the GF membrane not only had higher thermal stability and larger ionic conductivity but also provided Li–S cells with more stable capacity and better rate capability as compared to microporous PP membrane. It is, therefore, demonstrated that GF membrane with superior thermal stability and excellent electrolyte wettability is a promising separator candidate for high-performance Li–S batteries when it is used alone without the introduction of another PP layer. More importantly, the contribution of this manuscript to the scientific community is to provide a new route to further improve the electrochemical performance of Li–S batteries by using a simple GF membrane separator without introducing complex electrode structure designs, enhancing the practical application of Li–S batteries.

2. Experimental

2.1. Materials

Sulfur (S, 99.5–100.5%, Sigma-Aldrich), bis(trifluoromethane) sulfonamide lithium (LiTFSI, Sigma-Aldrich), lithium nitrite (99.99% trace metals basis, Sigma-Aldrich), n-butyl alcohol (99%, Sigma-Aldrich), N-methyl-2-pyrrolidone (NMP, 99%, Sigma-Aldrich), 1,3-dioxolane (DOL, Sigma-Aldrich), 1,2-dimethoxyethane (DME, Sigma-Aldrich), super P carbon black (C-65, TIMCAL Graphite & Carbon Ltd.) and polyvinylidene fluoride (Solef® PVDF-5130, Solvay) were used as received.

GF membrane (Whatman, thickness of 260 μm) made from borosilicate microfibers was investigated as the separator in this study. Microporous polypropylene (PP) separator (Celgard 2400, thickness of 25 μm) was used as a comparison to the GF membrane.

2.2. Structural characterization

The morphology of PP and GF separators was studied by using a field-emission scanning electron microscopy (FESEM, FEI Verios 460 L, USA).

The porosities of the separators were measured by conducting n-butyl alcohol uptake tests. In an uptake test, the porosity was calculated based on the following equation:

$$\text{Porosity (\%)} = (w_w - w_d) / (\rho_b \times V) \quad (1)$$

where w_w and w_d are the weights of wet and dry separators, respectively; ρ_b is the density of n-butyl alcohol, and V is the geometric volume of the separator.

2.3. Performance evaluation

The dimensional stability of the separators was determined by thermal shrinkage tests at 150 °C for 2 h. The electrolyte contact angle test was carried out by using a Canon EOS camera which was attached to a microscope (Meiji Techno America).

Liquid electrolyte uptakes were measured by soaking weighed separators in the liquid electrolyte of 1 M LiTFSI and 0.1 M $LiNO_3$ in a mixture of DOL and DME (1: 1 by volume) for 2 h at room temperature. The electrolyte uptake (EU) was then calculated by:

$$\text{EU (\%)} = (w_1 - w_0) / w_0 \times 100 \quad (2)$$

where w_0 and w_1 are the weights of the dry and wet separators, respectively.

Electrochemical impedance spectroscopy (EIS) was performed to investigate the ionic conductivity of liquid electrolyte-soaked separators by using Reference 600 Potentiostat/Galvanostat/ZRA (Gamry) over a frequency range from 1 MHz to 1 Hz under an AC voltage of 10 mV. During the measurement, the liquid electrolyte-soaked separators were sandwiched between two stainless steel electrodes. The ionic conductivity was calculated by using the following equation:

$$\sigma = L / (R_b \times A) \quad (3)$$

where L is the thickness of separator, A is the contact area between the separator and the stainless steel electrode, and R_b is the bulk resistance of the electrolyte, defined as the intercept of the semicircle with the real axis.

The electrochemical performance of Li–S cells containing PP and GF separators was evaluated by using coin-type cells. The sulfur cathode was prepared by mixing 70 wt% active material (S), 20 wt% Super P and 10 wt% PVDF binder in solvent NMP and coating the slurry onto the carbon-coated aluminum foil, following by drying at 60 °C in vacuum oven overnight to remove the solvent. Lithium metal foil was used as the anode. Li–S cells were assembled by sandwiching liquid electrolyte-soaked separator between lithium anode and sulfur cathode in an argon-fill glove box. The electrolyte used was the same as the one for electrolyte uptake measurement and its amount was controlled as 40 μL per 1 mg S. The areas of the electrodes and separator were 1.27 and 1.98 cm^2, respectively. The area of the GF separator was slightly larger than that of the electrodes to avoid the potential contact of the electrodes and the short circuit of the cells. A programmable battery cycler (Arbin Instruments) was used to record discharge/charge profiles and cycling performance with a voltage range between 2.8 V and 1.7 V vs. Li^+/Li at ambient temperature. Cyclic voltammetry (CV) measurements were carried out by using a Gamry reference 600 device with a scan rate of 0.1 mV s^{-1} in a potential range of 2.8–1.7 V. Several coin cells were disassembled in the charged state for further analysis after cycling. Morphological characterization of the lithium anodes before and after cycling was carried out with a field-emission scanning electron microscopy (FE-SEM, FEI Verios) after they were washed using DOL and dried in the argon-filled glovebox. The sulfur loading was around 0.7–1 mg cm^{-2} and all the cells' capacities were calculated based on the mass of sulfur.

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