Preparation of PVdF-based electrospun membranes and their application as separators

Yanhuai Ding\textsuperscript{1,2}, Ping Zhang\textsuperscript{1,2}, Zhilin Long\textsuperscript{1,2}, Yong Jiang\textsuperscript{1,2}, Fu Xu\textsuperscript{1,2} and Wei Di\textsuperscript{1}

\textsuperscript{1} College of Civil Engineering and Mechanics, Xiangtan University, Hunan 411105, People’s Republic of China
\textsuperscript{2} Institute of Fundamental Mechanics and Material Engineering, Xiangtan University, Hunan 411105, People’s Republic of China
E-mail: yhding@xtu.edu.cn

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Abstract
A one-step method preparing of poly(vinylidene fluoride)-based electrospun membranes (PEMs) containing TiO\textsubscript{2} has been developed. The effect of TiO\textsubscript{2} on the morphology, degree of crystallization and electrochemical behavior of PEMs was investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM), differential scanning calorimetry (DSC) and electrochemical measurements. The PEMs containing TiO\textsubscript{2} show improved ionic conductivity and cycling performance compared with pure PEMs.

Keywords: electrospun, morphology, ion conductivity, cycling performance

(Some figures in this article are in colour only in the electronic version.)

1. Introduction

Recently, microporous polymer electrolytes composed of electrospun membranes made of PVdF, P(VdF-HFP) and PAN have been developed by Lee and co-workers [1–4]. These electrospun membranes are composed of ultrafine fibers with diameters in the range of tens of nanometers to several micrometers. Among them, the PVdF electrospun membrane has received much attention due to its good ionic conductivity and high electrochemical stability in an organic electrolyte. However, the flexibility of PVdF is unsatisfactory due to its high crystallinity. It has been reported that the degree of crystallization of the polymer film decreases when it is filled with Al\textsubscript{2}O\textsubscript{3} nanoparticles [5]. In this paper, tetrabutyl titanate was used as the source of TiO\textsubscript{2} used to inhibit the crystallization of PVdF. The application of electrospun PVdF-based membranes for lithium ion batteries was also investigated.

2. Experiments

PVdF electrospun membranes were prepared using 20\% PVdF (Kynar\textsuperscript{TM}, 761, Atofina) solutions dissolved in mixed solutions of acetone/\textit{N}, \textit{N}-dimethylacetamide (7 : 3 by weight). For comparison, a PVdF/TiO\textsubscript{2} electrospun membrane was prepared. Tetrabutyl titanate, as the source of the TiO\textsubscript{2}, was added to the electrospinning solution (PVdF : TiO\textsubscript{2}, 95 : 5 by weight). The distance between the capillary tip and the collector was 15 cm and the applied voltage was 25 kV. All the membranes were heat-treated for 24 h at 100 °C in vacuum. The membrane thickness was maintained at 30 \(\mu\text{m}\). SEM (JEOL JSM-6700, Japan) and AFM (DI NS-3D, USA) were employed to characterize the morphology and microstructure of the PVdF-based electrospun membranes.

Test cells were assembled using Celgard\textsuperscript{TM} 2400 and the PVdF-based electrospun membranes as separators, lithium metal as an anode and LiFePO\textsubscript{4} as cathodes. Charge–discharge experiments were carried out on a lithium battery testing system (Lixin, China).
The ion conductivity was measured using the EIS method. The electrospun membranes were immersed into 1 mol $^{-1}$ LiPF$_6$-EC/DMC (1 : 1 by volume) for 60 min. After the excrecent solution at the surface of the polymer electrolyte was absorbed, the membranes were sandwiched between two symmetrical stainless-steel blocking electrodes. Using an FRD100 frequency response detector (AMETEK-AMT, USA), we measured the resistance of the polymer electrolyte. The frequency ranged from 1 Hz to 100 kHz, and the ac amplitude was 5 mV. The bulk resistance of the polymer electrolyte was determined from the impedance spectrum. Then, the ionic conductivity was calculated using the following equation:

$$\sigma = \frac{d}{R_b S}$$

Here, $\sigma$ is the ionic conductivity, $R_b$ is the bulk resistance; and $d$ and $S$ are the thickness and area of the specimen, respectively.

3. Results and discussion

SEM micrographs of the PVdF-based microporous membranes are shown in figure 1. It is clearly observed that the average fiber diameter of the PVdF electrospun membrane was over 150 nm. For comparison, the average fiber diameter of the PVdF/TiO$_2$ electrospun membrane was about 100 nm. Furthermore, the pore size of the PVdF/TiO$_2$ electrospun membrane was smaller than that of the PVdF electrospun membrane. An interesting feature can be seen in the figure, the nanofibers in the PVdF/TiO$_2$ electrospun membrane are connected to each other to form an interconnecting network. It has been reported that interconnected nanofibers may provide greater mechanical strength, and lower elongation and tensile modulus than unattached nanofibers [1]. When the tetrabutyl titanate is added to the PVdF polymer solution, the fibrous structure is not retained and the fiber diameter decreases.

The detailed morphology of the PVdF/TiO$_2$ electrospun membrane was examined by AFM. An AFM image of the PVdF/TiO$_2$ electrospun membrane is shown in figure 2. The apparent pore size of the PVdF/TiO$_2$ electrospun membrane was about 500 nm. A three-dimensional web structure was formed by the interconnected ultrafine fibers, which indicated that the interstices were also fully interconnected. The uptake of the electrolyte solution was determined from the pore size, porosity and specific surface area. The apparent porosity of the electrospun membranes was characterized using the BuOH uptake method. The results showed that the apparent porosities of the PVdF and PVdF/TiO$_2$ electrospun membranes reached 81 and 85%, respectively. The uptakes of electrolyte solution for the PVDF and PVdF/TiO$_2$ electrospun membranes were about 338 and 367%, with leakages of electrolyte solution (after 60 min) of about 11 and 8%, respectively. The absorption of electrolyte solution in the PVdF-based electrospun membranes was higher than that in commercially available polyolefin separators. The higher electrolyte affinity of the PVdF-based electrospun membranes can be attributed to the higher specific surface area, higher porosity and unique tortuosity of the pore structure.
Figure 2. The AFM images of PVdF/TiO$_2$ electrospun membrane.

Figure 3. The DSC curves of the electrospun membranes.

Figure 4. The ion conductivity of electrospun membranes.

Figure 5. The first charge–discharge curves of testing cells.

The DSC curves of the electrospun membranes are shown in figure 3. The curves have similar shapes with an endothermic peak from 150 to 180 °C and a melting point at 170 °C. It has been calculated that the degree of crystallization of PVdF/TiO$_2$ was lower than that of raw PVdF, which can be attributed to the fact that the motion of polymer segments is hindered by the hydrogen bond between the OH groups (on the surface of TiO$_2$) and the fluorine (in the polymer chains) [5].

The temperature dependence of the ionic conductivities of the electrospun membranes over a temperature range of 20–65 °C is presented in figure 4. The ionic conductivities of the PVdF and PVdF/TiO$_2$ electrospun membranes were $0.89 \times 10^{-3}$ and $1.4 \times 10^{-3}$ S cm$^{-1}$ at 25 °C, respectively. At 60 °C, the ionic conductivities reached $3.3 \times 10^{-3}$ and $3.0 \times 10^{-3}$ S cm$^{-1}$, respectively. The high ionic conductivity can be mainly ascribed to the porous structure of the electrospun membranes because Li ions are mostly transferred through the electrolyte solution. The unique pore structure of the electrospun membranes results in the high absorption ability of the electrolyte solution [2, 3]. The ionic conductivity increased slightly after the PVdF was filled with TiO$_2$, which also caused a decrease in the degree of crystallization, thereby inducing an increase in the amorphous swollen fibrous phase. This phase contributed to the formation of more tunnels allowing greater Li$^+$ migration.
Prototype cells using Celgard™ 2400 and the PVdF-based electrospun membranes were fabricated and subjected to cycle tests with cut-off voltages of 2.4 and 4.1 V at a constant current rate of 0.1C. Figure 5 shows the first charge–discharge curves of the test cells at room temperature. All the curves show a stable charge–discharge platform, and the specific discharge capacities are in the range of 143–148 mAh g\(^{-1}\). The cycling performances of the test cells are presented in figure 6. After 20 cycles, the capacity losses of the test cells were 4.34% (PVdF/TiO\(_2\)), 6.49% (PVdF) and 10.68% (Celgard™ 2400). The improved cycling performance of the test cells with the PVdF-based electrospun membranes can be ascribed to the reduced leakage of the electrolyte solution.

4. Conclusion

PVdF/TiO\(_2\) separators for lithium ion batteries with a high-specific surface area and high porosity were prepared using electrospun technology with tetrabutyl titanate as the source of the TiO\(_2\). After filling the PVdF with TiO\(_2\), the ionic conductivity and cycling performance of the PVdF electrospun membranes were improved. The ionic conductivity of the PVdF/TiO\(_2\) electrospun membranes reached 1.4 × 10\(^{-4}\) S cm\(^{-1}\) at room temperature. The capacity loss of the test cells with the PVdF/TiO\(_2\) electrospun membranes was only 4.34% after 20 cycles.

Acknowledgments

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