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Composite gel polymer electrolyte with ceramic particles for $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-$Li_4Ti_5O_{12}$ lithium ion batteries

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ABSTRACT

In this study, a composite polymer matrix for gel polymer electrolyte (GPE) is prepared by the electrospinning process, combining poly(vinylidene fluoride-co-hexafluoropropylene) and nano-sized Al_2O_3 ceramic particles. The composite matrix is impregnated with a liquid electrolyte to prepare the GPE-Al_2O_3 composite and its properties are compared with those of pure GPE. The GPE-Al_2O_3 composite improves the interfacial resistance, ion coordination and the electrochemical stability of the GPE. The electrochemical performances are analyzed by applying the GPEs to $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) and $Li_4Ti_5O_{12}$ (LTO) cells. The GPE-Al_2O_3 composite exhibits a higher discharge capacity than the GPE at 0.1 C-rate and excellent performance in both the LTO and the NMC half-cells under cyclic conditions. The GPE-Al_2O_3 composite shows good compatibility and high electrochemical property on LTO/NMC full-cell.

1. Introduction

Polymer electrolytes have been widely used in the development of high-performance lithium ion batteries with improved safety. Even though commercial liquid electrolytes provide excellent ionic conductivity, they exhibit safety-related issues, which can be overcome by the use of polymer electrolytes [1]. In the case of gel polymer electrolytes (GPEs), a polymer matrix is prepared first to absorb the liquid electrolyte. Subsequently, the liquid electrolytes are absorbed into the polymer matrix and they occupy the pores. The absorbed liquid electrolyte is immobilized in the pore and becomes stabilized, retaining the properties of the liquid electrolyte and the separator. The ion mobility in the polymer matrix is significantly increased by the absorption of the liquid electrolyte, resulting in high ionic conductivity. The polymer matrix can be prepared by various methods such as casting, phase inversion, and electrospinning. Among them, the electrospinning process is most efficient in providing high porosity and uniform pores on both the top and bottom layers. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) has been extensively used as a polymer matrix due to its high mechanical strength and electrochemical stability [1–3].

Incorporation of ceramic particles into the polymer matrix improves not only the ionic conductivity and mechanical strength of the GPE, but also its compatibility with lithium metal electrodes. Further, additional spaces are formed between the polymer and the ceramic particles, increasing the uptake of the liquid electrolyte and accordingly the ionic conductivity. In addition, ceramics such as Al_2O_3 possess a high dielectric constant, which helps in capturing anions in the liquid electrolyte and transferring lithium ions without coordinating with the anions. However, high amounts of ceramic particles decrease the ionic conductivity as the transportation of the ions is disrupted. The optimum concentration of ceramic particles for GPEs was reported to be 6 wt.% [4–11].

In this study, composites of PVdF-HFP with 6 wt.% Al_2O_3 ceramic particles were prepared as fibrous matrices by electrospinning. The polymer matrices were converted to the GPEs by the absorption of liquid electrolyte. The physical and electrochemical performances of the polymer matrix with and without the addition of the ceramic particles were compared. Electrodes of $Li_4Ti_5O_{12}$ (LTO) and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) together with the GPE-Al_2O_3 composite were applied to lithium polymer batteries. The GPE-Al_2O_3 composite exhibited good electrochemical stability and compatibility with both the LTO anode and the NMC cathode.

2. Experimental

2.1. Preparation of PVdF-HFP fibrous membranes and gel polymer electrolytes

The polymer solution of PVdF-HFP (Kynar Flex 2801, $M_w = 477 \times 10^5$, VdF/HFP ratio: 88/12, Elf Atochem) was vacuum-dried at

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80 °C for a day. A solution consisting of Al_2O_3 ceramic particles and acetone/N,N-dimethylacetamide (7/3, w/w) was prepared for producing the fibrous membranes. The polymer matrix was prepared by electrospinning the polymer solution mixed in acetone/N,N-dimethylacetamide (7/3, w/w) solution at an applied voltage of 18 kV at room temperature. The polymer matrix with Al_2O_3 was prepared by adding 6 wt.% of vacuum-dried Al_2O_3 ceramic particles to the polymer solution and electrospinning under the same condition as that of the PVdF-HFP matrix. The as-prepared membranes were vacuum dried at 60 °C for 12 h [4]. The polymer matrices were impregnated with the required quantity of 1 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC)/dimethyl carbonate to form the GPE.

2.2. Characterization

The morphologies and elemental compositions of the prepared polymer matrices were studied using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The crystallinities of the membranes were determined by analyzing the X-ray diffraction (XRD) patterns. Raman spectra of the two GPEs were recorded on a Bruker FRA 106/S Fourier-transform spectrometer. The uptakes of the polymer matrixes were evaluated by using liquid electrolyte in an argon atmosphere. The electrochemical stabilities of the GPEs were measured by the linear sweep voltammetry (LSV) method at an interval of ~12 h and a scan rate of 0.1 mV s^{-1}. The ionic conductivities and interfacial resistances of the GPEs were measured by *ac* impedance analysis. Both the prepared GPEs were applied to Li/GPE/NMC and Li/GPE/LTO cells and the electrochemical performances of the cells were measured. The NMC electrode, which is the anode active material, consisted of super-P carbon, PVdF, and binder in the ratio 89:7:4 (wt.%) and the LTO electrode, which is the cathode active material, consisted of super-P carbon, PVdF, and binder in the ratio 80:10:10 (wt.%). The electrochemical testing of the cell was performed using a constant current charge/discharge device in the voltage range of 1–2.5 V for LTO and 3.5–4.2 V for NMC at a current density of 0.1 C-rate at 25 °C. The cells were assembled in a glove box filled with Ar gas containing water content less than 10 ppm [4].

3. Results and discussion

The morphologies of the polymer matrices with the respective fiber diameters are shown in Fig. 1. It can be seen that both the matrices consist of fibers with pores, which can increase the absorption of the liquid electrolyte. The surface morphology of the Al_2O_3-composite polymer matrix is smoother than the pure polymer matrix. The average diameter of the fiber is 2.3 μm for the pure polymer matrix (Fig. 1(a) and (b)) and 1.2 μm for the Al_2O_3 composite polymer matrix (Fig. 1(c) and (d)). The smooth surface morphology and the reduced fiber diameter are attributed to the presence of the ceramic particles in the polymer matrix, which prevent shrinkage and aggregation of the polymer. Smooth surfaces and thin fibers are beneficial for the formation of uniform pores.

Fig. 2 shows the distributions of the elements in the electrospun pure polymer matrix and the Al_2O_3-composite polymer matrix as obtained by the SEM-EDS measurements. The pure polymer matrix (Fig. 2(a)) shows the presence of only carbon atoms (Fig. 2(b)). The Al_2O_3 composite polymer matrix (Fig. 2 (c)) consisted of carbon (Fig. 2(d)), aluminum (Fig. 2(e)), and oxygen (Fig. 2(f)), and all the elements were distributed homogeneously in the polymer fibers.

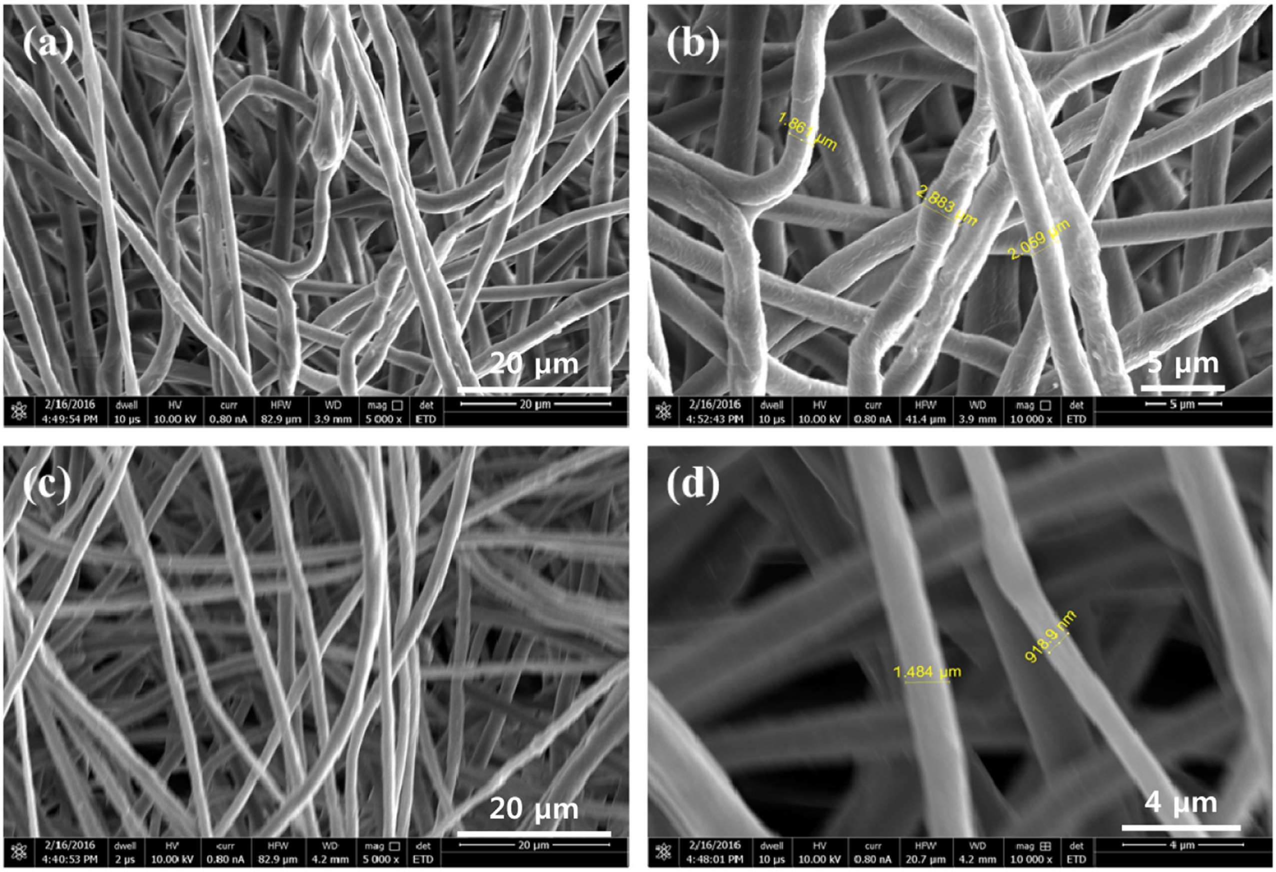

Fig. 1. SEM images of (a, b) pure GPE and (c, d) Al_2O_3-composite GPE.