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Self-supported PVdF/P(VC-VAc) blended polymer electrolytes for $LiNi_{0.5}Mn_{1.5}O_4$/Li batteries

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ABSTRACT

New **s**elf-supported poly(vinylidene fluoride)/poly (vinyl chloride-co-vinyl acetate) (PVdF/P(VC-VAc)) blended polymer membranes are prepared via a phase inversion method, and then their electrochemical performances, immersed in the liquid electrolyte as the polymer electrolyte for lithium-ion batteries (LIBs), are evaluated. The Fourier transform infrared spectroscopy analysis, the differential scanning calorimeter test and the X-ray diffraction measurement demonstrate that homogeneous PVdF/P(VC-VAc) polymer composites can form at all blend compositions and the crystallinity degree of the blended polymers decreases as the P(VC-VAc) content increases. Specifically, when the proportion of PVdF/P(VC-VAc) is 70:30 (wt%), membranes with a rich surface and internal porous structure can be acquired. The ionic conductivity of the polymer electrolyte achieves a maximum value of 3.57 mS cm^{-1} at room temperature, and favourable electrochemical performances of LIBs can be obtained. $LiNi_{0.5}Mn_{1.5}O_4$/Li cells with the as-prepared polymer electrolyte exhibit a higher initial discharge capacity of 131.0 mAh g^{-1} and superior cycle stability with a capacity retention of 96.1% at 0.2 C after 200 cycles compared to cells based on pure PVdF and P(VC-VAc) membranes. This can be attributed to the superior compatibility of the electrolyte with the electrodes. The results also indicate this electrolyte has promising applications in high-voltage LIBs.

1. Introduction

The separator is an indispensable part of lithium ion batteries (LIBs). It plays a crucial role in insulating the anode and cathode to prevent short-circuiting and allows for the rapid transfer of lithium ions [1]. Currently, conventional polyethylene (PE) and polypropylene (PP) separators dominate the commercial LIB market because of their advantages. However, PE and PP still have some drawbacks, including the wide use of flammable organic liquid electrolytes in the LIBs, poor compatibility with liquid electrolytes due to their hydrophobic properties, and high manufacturing cost [2–4]. The surface modification of PE or PP with gel polymer electrolytes should be able to enhance their compatibility and safety performance. In fact, several works have demonstrated that modified separators with a polymer matrix to fix the solvent exhibit a higher electrochemical stability, mechanical strength and thermal stability [5–7]. However, these modified PE and PP separators are still expensive because of their delicate manufacturing processes. Thus, researchers are attempting to develop novel separators prepared from low-cost, non-polyolefin materials with a simple technique.

Poly(vinylidene fluoride) (PVdF), poly(ethyleneoxide), carboxymethyl cellulose and hydroxyethyl cellulose have been reported as alternative separators that can substitute for PE or PP [8–11]. Specially, PVdF has attracted considerable attention because it has good film forming properties, a high affinity for the liquid electrolyte and high electrochemical stability [12–15]. However, prepared PVdF-based membranes suffer from low ionic conductivity that is restricted by the high crystallinity of PVdF [16]. Attempts to solve this problem have included innovative polymer synthesis [17,18], blending of two polymers [19,20], and synthesis of composite polymer electrolytes by addition of inorganic fillers [21,22]. Of the mentioned techniques, blending has been identified as a simple and effective method because of the ease in preparation and property control of polymer electrolytes by changing the composition of the blended polymers. For example, the copolymer poly(vinylidene fluoride-co-hexafluoropropene) (P(VdF-HFP)) is also a semi-crystalline polymer with a degree of crystallinity significantly reduced due to the addition of hexafluoropropylene (HFP) [23]. Hence, it shows high flexibility as compared to PVdF. Kim et al. prepared PVdF-HFP/PAN polymer blend membranes, and high ionic conductivity and good mechanical properties were observed for the gel polymer electrolytes [24]. PEO/PVdF blends was prepared by Xi et al. and

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the result showed that the addition of PEO can obviously improve the pore configuration of membranes, and the highest porosity of about 84% and ionic conductivity of about 2 mS cm^{-1} can be obtained [25]. Nunes-Pereira as well as Carlos also had a system describe on the PVdF based polymer separators, which indicates a good developing tendency for this electrolyte applied in LIBs [26,27].

The poly(vinyl chloride) (PVC)-based polymers are deemed to be the most promising polymer candidates for polymer electrolytes and have attracted attention from researchers because of their satisfactory conductivities (~10^{-3} S cm^{-1}) [28,29]. However, PVC-based electrolytes were found to suffer from solvent exudation. The poly(vinyl acetate) (PVAc) is also commonly used as the matrix for polymer electrolytes based on its low glass transition temperature, good mechanical stability and easy film formation properties, but its ionic conductivity seem to be undesirable (< 10^{-3} S cm^{-1}) [30,31]. Although efforts were exerted to ameliorate these problems, for example, blending with other polymers or plasticizer combinations, the performance of LIBs using these electrolytes still need further improvement [32,33]. Thus, we try to formulate the poly (vinyl chloride-co-vinyl acetate) (P(VC-VAc)) which contains the –VC and –VAc units to be blended with PVdF for preparing polymer electrolytes via phase-inversion method. Generally, the performance of the membrane for battery applications are strongly influenced by porosity, processing technique and polymer matrix due to its influence in the specific surface available for liquid electrolyte adsorption and lithium ion transport [34]. The present approach has obvious predominance in improvement of electrolyte property, on the one hand, the P(VC-VAc) is a typical amorphous polymer which may contribute to decreasing the crystallinity of blended system, on the other hand, the phase-inversion process (using solvent and non-solvent system) is very effective at promoting the porosity of the membrane [35,36]. Therefore, to obtain a polymer electrolyte of good ionic conductivity with high uptake ratio is a promising work herein. And especially the prepared electrolytes are tentatively used in the high voltage lithium ion batteries since the solvent absorbed in the matrix is known to be helpful for promoting the plasticization of polymer materials which conduce to improving the interfacial stability between the electrolytes and electrodes [7]. The effects of these polymer electrolytes on the performance of LIBs were evaluated by linear sweep voltammetry, electrochemical impedance spectroscopy and charge-discharge tests.

2. Experimental

2.1. Preparation of PVdF/P(VC-VAc) membranes and polymer electrolytes

The polymer membranes were prepared by the phase inversion method. PVdF (MW: 130,000, Arkema Shanghai Co., Ltd.) and P(VC-VAc) (MW: 52,000, Kaneka Trading (Shanghai) Co., Ltd.) were dissolved (10 wt%) in a mixture of tetrahydrofuran (THF) and N,N-dimethyl formamide (DMF) (THF:DMF=7:3, in weight) and stirred for 8 h at 30 °C. Then, the viscous slurry was cast onto a glass plate using a doctor blade and subsequently immersed in deionised water for phase inversion. The PVdF/P(VC-VAc) blended polymer membranes had a final thickness of approximately 130 µm and were obtained after drying the wet membranes at 50 °C for 72 h in a vacuum. The polymer electrolytes were obtained by soaking the membranes in the liquid electrolyte in an argon-filled glove box. The liquid electrolyte is 1.0 mol L^{-1} $LiPF_6$ in a mixed solvent of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (EC:DMC:EMC=1:1:1 by volume, battery grade, Guangzhou Tinci Material Technology Co., Ltd.). For simplicity, P0, P10, P30, P50, P70, P90 and P100 designate the membranes or electrolytes with P(VC-VAc) to PVdF weight ratios of 0:100, 10:90, 30:70, 50:50, 70:30, 90:10, and 100:0, respectively.

2.2. Characterisation of PVdF/P(VC-VAc) membranes and polymer electrolytes

The surface morphology of the membranes was characterised by scanning electron microscopy (SEM) (ZEISS Ultra 55, Germany) at an acceleration voltage of 5 kV. Glass transition temperatures (T_g) and melting temperatures (T_m) of the polymer membranes were measured using a differential scanning calorimeter (DSC) (Q20, TA Instruments-Waters LLC). Each sample was scanned from −60 to 200 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The thermal behaviour of the polymer membranes was studied by thermogravimetric analysis (TGA) (STA449F3, Netzsch, Germany) from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. X-ray diffraction (XRD) measurements were used to analyse the crystal structures of the prepared membranes by an X-ray diffractometer (Bruker D8 Advance, Germany). Fourier transform infrared (FTIR) spectroscopy was carried out using an FTIR spectrometer (Nicolet 6700, United States). Mechanical strength measurements were carried out on Electromechanical Universal Testing Machine (CMT 6104, MTS Systems (China) Co., Ltd) at a tensile speed of 50 mm min^{-1} longitudinally at room temperature. The sample dimensions were 80 mm×10 mm.

To measure the porosity of the membranes, the membranes were immersed into n-butanol for 2 h, and then the porosity (P) was calculated using Eq. (1):

$$P = (m_a/\rho_a)/(m_a/\rho_a + m_p/\rho_p) \tag{1}$$

where ρ_a and ρ_p are the densities of n-butanol and the dry membrane, respectively, and m_a and m_p are the masses of the n-butanol incorporated in membrane and the dry membrane, respectively.

To measure the uptake of the membranes, the membranes were immersed in 1 M $LiPF_6$-EC/DMC/EMC electrolyte for 15 min in a glove box, and then, the electrolyte uptake was calculated using Eq. (2):

$$A(\%) = (W_2 - W_1)/W_1 \times 100\% \tag{2}$$

where W_1 is the weight of the dry membrane and W_2 is the weight of wet membrane after immersion in the above electrolyte.

The ionic conductivity of the polymer electrolytes was determined by a symmetrical cell using electrochemical impedance spectroscopy (EIS). The polymer electrolytes were sandwiched between two circular stainless steel electrodes. Impendence data were obtained on the Instrumental Electrochemical Workstation (CHI660, Chenhua, Shanghai) with a potential amplitude of 5 mV from 100 kHz to 1 Hz. The ionic conductivity was calculated based on the bulk electrolyte resistance (R) according to Eq. (3):

$$\Sigma = L/(S\cdot R) \tag{3}$$

where L is the thickness of the membrane and S is the contact area between the polymer electrolyte and the stainless steel electrodes.

The electrochemical stability of the polymer electrolyte was evaluated by measuring the oxidation decomposition potential of the electrolyte on a stainless steel electrode by linear sweep voltammetry (LSV) using lithium foils as the counter electrode and reference electrode. The interfacial compatibility with the lithium electrode was determined by EIS on a lithium foil electrode using Li/polymer electrolytes/Li cell.

2.3. Electrochemical measurements

To evaluate the cell performances with the PVdF/P(VC-VAc) based polymer electrolytes, the coin cells were assembled with $LiNi_{0.5}Mn_{1.5}O_4$ (China, XingNeng New Materials Co., Ltd.) as the cathode active material and lithium foil as the anode. The $LiNi_{0.5}Mn_{1.5}O_4$ electrode was prepared by mixing 80.0 wt% $LiNi_{0.5}Mn_{1.5}O_4$, 10.0 wt% carbon, and 10.0 wt% binder PVDF and then coating the slurry onto an Al foil. Charge-discharge testing was conducted on battery test system (CT-3008, Neware, China) between 3.5 V and 5.0 V at room temperature.