



Preparation of hybrid polymer based on polyurethane lithium salt and polyvinylidene fluoride as electrolyte for lithium-ion batteries



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ABSTRACT

In this paper, hybrid microporous gel polymer electrolytes (HMGPEs) based on polyvinylidene fluoride (PVdF)/polyurethane lithium salt (PLS) are fabricated by thermal phase separation technique. PLS is synthesized via condensation copolymerization of polyethylene glycol 800 (PEG800) and diphenylmethane-diisocyanate (MDI), and then neutralized with LiOH. The effect of PLS on the morphologies of the hybrid membrane, electrochemical properties and cycle performance of the assembled polymer lithium-ion rechargeable batteries are studied in detail. The morphologies of the hybrid polymer membranes are examined by scanning electron microscope (SEM). The intercalation of PVdF/PLS hybrid membranes is characterized by X-ray diffraction (XRD), differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA). The incorporation of PLS in PVdF matrix can enhance ionic conductivities and electrochemical stabilities for the prepared HMGPEs. The assembled lithium-ion batteries based on HMGPEs with weight ratio 80:20 of PVdF and PLS (PVdF/PLS-20) delivers the highest charge-discharge capacity (about 175mAh g⁻¹), and the cell based on HMGPEs of with weight ratio 90:10 of PVdF and PLS (PVdF/PLS-10) shows the best stability in cycle performance.

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1. Introduction

Polymer electrolytes have received considerable attention for application in lithium-ion batteries (LIB), fuel cells, super capacitors, etc. [1,2]. Several polymer materials such as poly(vinylidene fluoride) (PVdF), polyacrylonitrile (PAN), polyvinyl chloride (PVC), poly(methyl methacrylate) (PMMA) and polyurethane (PU), have been used as the host polymers for preparation of polymer electrolytes [3–5]. PVdF is a well-known semi-crystalline thermoplastic polymer with excellent film-forming ability and thermal stability [6]. PVdF with the fluorine atoms in the backbone structure has a high dielectric constant, which is useful in dissociating lithium salt and conducting lithium-ions in the polymer electrolyte. Due to the high resistance and good chemical stability, PVdF becomes a favorable polymer matrix for gel polymer electrolyte in lithium-ion batteries [3]. But the main problem is PVdF-based gel polymer electrolyte tends to the leakage of liquid electrolyte due to the phase separation between polymer matrix and the absorbed liquid

electrolyte. The defect limits the application of pure PVdF-based polymer electrolyte in lithium batteries [7].

In recent years, there have been many efforts to develop polymer electrolytes with large absorption of electrolyte, high conductivity and stable electrode/electrolyte interfacial properties with minimum resistance in ionic diffusion [8,9]. Compared with the traditional separator used, the battery assembled with HMGPEs has no free liquid electrolyte. The HMGPEs have higher porosity, better wettability and retention of the electrolyte. Because of the higher porosity of HMGPEs, the electrolyte uptake and ionic conductivity are improved. The preparation methods for polymer electrolytes include blending, polymerization, crosslinking, and nanofillers or ionomers to form composite polymer electrolyte [10–14]. Composite polymer gel electrolyte based on microporous polymer membrane has received great attention in polymer lithium-ion batteries due to its simple fabrication, high ionic conductivity and good compatibility with electrodes. C.H. Kim et al. [15] reported a new plasticized polymer electrolyte based on the ionomer, poly(methylmethacrylate-co-lithium maleate), presented improved electrochemical properties. Y.S. Zhu et al. [16] synthesized a novel single-ion conducting polymer electrolyte (LiPAAOB) which ionic conductivity reached $2.3 \times 10^{-6} \text{ S cm}^{-1}$ at

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ambient temperature. These results presented that the ionomer has potential application in polymer lithium-ion batteries.

Hybrid microporous gel polymer electrolytes (HMGPEs) will be expected better electrochemical performance by combining ionomer, such as polymer lithium salts (PLS), in the polymer matrix. In this paper, a novel PLS is synthesized and the performance of PVdF-based HMGPEs is investigated. The hybrid microporous polymer membranes are prepared by thermal phase inversion, and then the membranes are activated after the absorption of organic liquid electrolyte. The morphology, stability, conductivity and electrochemical properties of the as-prepared HMGPEs are studied in detail.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVdF, M_n , ca. 4×10^5 ; M_w , ca. 7.96×10^5 ; $M_w/M_n = 1.99$, Shanghai Ofluorine Chemical), LiOH and polyethylene glycol 800 (PEG 800) (Sinopharm Chemical) were dried under vacuum at 80°C for 24 h. Diphenyl-methane-diisocyanate (MDI) was used as received (Wanhua Chemical). 1.0 M organic liquid electrolyte (1 M LiPF_6 in ethylene carbonate (EC)/propylene carbonate (PC)/dimethyl carbonate (DMC) (1:1:1, v/v/v)) was supplied by Guotai-Huarong New Chemical Materials Co., Ltd. N,N-dimethylformamide (DMF) (A.R.) and glycerin (A.R.) which were used as received.

2.2. Preparation of polyurethane lithium salt (PLS)

The fabrication process of PLS is schematically illustrated in Scheme 1. Firstly, PEG800 and MDI were dissolved in DMF at mole ratio of 1:1.1, the mixture were kept stirring for 6 h at 75°C under nitrogen atmosphere. A small amount of LiOH dissolved into THF/methanol solution was doped into the mixture. The mixed reactants stirred 8 h at 75°C . Finally, the solution was poured into a glass dish and the product was dried under normal pressure at 180°C for 12 h and then under vacuum at 150°C for another 24 h to absolutely remove the solvent.

2.3. Preparation of PVdF-based hybrid microporous membrane

PVdF/PLS based hybrid microporous membranes were prepared by thermal phase separation method. A proper amount of PVdF and PLS (100:0, 95:5, 90:10, 80:20 by weight ratio) were dissolved in a mixture solution of DMF and glycerin (8:1 by volume), and stirred for 12 h at room temperature. The polymer solution was cast onto a glass plate through a scraper, and the as-produced film was dried at 80°C for 24 h under vacuum. The thickness of the film is adjustable by the scraper. During this process, DMF and glycerin evaporated in turn (the boiling point of DMF is lower than glycerin), and the micropores in the membrane was formed. For convenience, the obtained hybrid microporous membranes were simply named as PVdF/PLS-X while X is 5, 10, and 20 based on the starting weight ratio of PLS to the blending polymers.

2.4. Characterization

The surface morphologies of the hybrid microporous membranes were examined by field emission scanning electron microscope (FE-SEM, SIGMA, ZEISS). FTIR measurements were carried out on BRUKER VECTOR-22 spectrometer at room temperature. X-ray diffraction patterns of the hybrid microporous membranes were performed by using D/MAX-RA X-ray diffractometer (Rigaku). DSC measurements were carried out by using Q100 (TA Instruments, USA) over the temperature of 30

to 200°C at a scan rate of 10°Cmin^{-1} . The experimental specimens (8–10 mg) were dried at 60°C under vacuum for 24 h before being measured. All the thermograms were base line corrected and calibrated according to Indium metal. The crystallinity (χ_c) was calculated based on the following Equation (1):

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^*} \quad (1)$$

Where the ΔH_f and ΔH_f^* represent the fusion enthalpy of hybrid microporous membrane and pure PVdF with 100% crystallinity, respectively.

2.5. Porosity and electrolyte uptake measurement

The porosity (P) of the dried hybrid microporous membranes were investigated by immersing the membranes into n-butanol for 2 h and then calculated according to Equation (2):

$$\text{Porosity}(\%) = \frac{m_a/\rho_a}{m_a/\rho_b + m_b/\rho_p} \times 100 \quad (2)$$

where, ρ_a and ρ_b are the density of n-butanol and the dry hybrid microporous membrane, respectively, m_a and m_b are the mass of the swollen membrane and the dried membrane, respectively.

The ability of electrolyte uptake for different hybrid microporous membranes was determined by measuring weight increment and calculated according to the following Equation (3):

$$\text{Uptake}(\%) = \frac{W - W_0}{W} \times 100 \quad (3)$$

where W_0 and W are the weights of dried membranes and swollen membranes, respectively.

2.6. Electrochemical measurement

The electrochemical cell of SS/HMGPE/SS was assembled by sandwiching HMGPE between two stainless steel (SS) blocking electrodes. The conductivity was measured recording to AC impedance spectra by using PARST 2273 electrochemical workstation at the frequency range of 100 KHz–100 mHz and the amplitude of 5 mV. The HMGPE film was about $40 \mu\text{m}$ in thickness and 0.64 cm^2 in the area. The lithium-ion transference number (t_{Li^+}) was measured by using asymmetric cell of Li/HMGPE/Li according to DC polarization combined with AC impedance method as described by Bruce and Vincent [17,18]. It was calculated by Equation (4):

$$t_{\text{Li}^+} = \frac{I_s(\Delta V - R_s I_0)}{I_0(\Delta V - R_0 I_s)} \quad (4)$$

where I_0 and I_s are the initial and steady current, respectively; R_0 and R_s are the initial interfacial and steady-state resistance, respectively; ΔV is the applied DC voltage.

The electrochemical stability was measured by a linear sweep voltammetry (LSV) using a stainless steel working electrode and lithium foil as the counter (Li/HMGPE/SS) at the scanning rate of 5 mV s^{-1} from the voltage of 2 to 6 V by PARST 2273 electrochemical analyzer.

The charge-discharge tests of the Li/CMGPE/LiCoO₂ were carried out by using Land Battery Test System (Wuhan Land Electronic Co. Ltd. China). A mixture composed of 80 wt.% LiCoO₂ powder (DLG Battery Co. Ltd., China), 10 wt.% carbon black, and 10 wt.% poly(vinylidene fluoride) (PVdF) were mixed with N-methyl-2-pyrrolidone (NMP). The slurry was spread onto aluminum foil substrates and dried at 120°C for vacuum. The electrode was mounted as the positive electrode versus lithium metal as the anode in CR 2016 coin-type cells. The cell was assembled by sandwiching HMGPE between lithium anode and LiCoO₂ cathode (LiCoO₂/HMGPE/Li) in an argon-filled glove box. Charge-discharge

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