



Effect of urea as pore-forming agent on properties of poly(vinylidene fluoride-co-hexafluoropropylene)-based gel polymer electrolyte



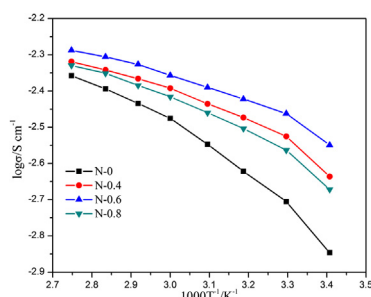
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HIGHLIGHTS

- P(VDF-HFP)-based GPE using urea as pore-forming agent was prepared by phase inversion method.
- The GPE with 0.6 g urea show the smoothest surface morphology with ionic conductivity at room temperature about 2.671 mS cm^{-1} .
- Mechanism of ionic conductivity follows Arrhenius relationship and interfacial performance gains much improvement.
- The assembled Li/GPE/LiCoO₂ coin cell shows good rate and cycle performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP))-based gel polymer electrolyte (GPE) membranes are prepared by phase inversion method using urea as pore-forming agent and dimethylformamide as solvent, respectively, and the desired polymer electrolytes are obtained after being immersed the as-prepared polymer electrolyte membranes into liquid electrolytes for 1 h. Physico-chemical properties of the GPEs are investigated by SEM, XRD, FT-IR, TG-DSC, EIS and LSV. When the weight ratio of urea to P(VDF-HFP) is up to 0.6:4, the results show that the polymer electrolyte membrane presents the most uniform surface with abundant interconnected micro-pores and excellent thermal stability, in which the ionic conductivity at room temperature can reach 2.671 mS cm^{-1} and the reciprocal temperature dependence of ionic conductivity follows Arrhenius relationship. The interfacial resistance of the Li/GPE/Li simulated cell with 0.6 g urea can rapidly increase to a steady value about $650 \Omega \text{ cm}^{-1}$ from the initial value about $475 \Omega \text{ cm}^{-1}$ during 15 days storage at $30 \text{ }^\circ\text{C}$. The polymer electrolyte with 0.6 g urea can be stable at 5.3 V (vs Li/Li⁺) at room temperature and the assembled Li/GPE/LiCoO₂ coin cell can also show good rate and cycle performance.

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1. Introduction

Recently, more and more attention has been focused on the gel polymer electrolytes (GPEs) for their potential applications in lithium ion battery owing to their lack of leakage, high flexibility

and good interfacial compatibility with electrodes [1,2]. It is worthy to note that the safety performance of the lithium ion battery with GPEs gains much improvement because the GPEs with few free-flowing liquid electrolytes can prevent combustions and explosions from decomposition of the liquid electrolytes in some extreme conditions. Generally, GPE is mainly composed of polymer matrix, entrapped liquid electrolytes and suitable additives. Among the numerous polymer matrices studied, the copolymer of vinylidene fluoride and hexafluoropropylene (P(VDF-HFP)) is considered

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to be the most potential matrix material, because it has relatively lower crystallinity due to the copolymerization effect between VDF and HFP in comparison with poly(vinylidene fluoride) (PVDF) [3–5]. In addition, HFP amorphous phase can facilitate high ionic conduction and VDF crystalline phase can act as a mechanical support for the polymer electrolytes [5]. The mainstream preparation method of GPEs is phase inversion technique, mainly including the processes of fabricating and activating the porous polymer electrolyte membranes [6,7]. It is well known that the more the micro-pores are, the higher the electrolyte uptake ratio is. In other words, the rich micro-pores can enhance the ionic conductivity of the polymer electrolytes. Therefore, fabricating polymer electrolyte membranes with porous structure becomes the focal topic in the field of the polymer electrolytes for lithium ion battery. Since the supercritical carbon dioxide was successfully used to prepare porous polymer membrane, more and more pore-forming agents, such as polyvinyl pyrrolidone, polyethylene glycol and salicylic acid, are employed to enhance ionic conductivity of polymer electrolytes by improving the micro-pore structure of the porous polymer membranes [4,8–11]. Urea, easily decomposing into carbon dioxide and ammonia gas at increasing temperature, is a novel pore-forming agent to fabricate porous polymer electrolyte membranes [12]. However, some properties reported by Chen, such as thermal stability and electrochemical working window, decrease with adding urea into polymer electrolyte membranes, while the ionic conductivity and interfacial stability gain improvement, which can be attributed to the poor mechanical properties of the copolymer matrix P(AN-MMA-ST) [13]. In the present work, P(VDF-HFP) is selected as polymer matrix to fabricate the polymer electrolytes using urea as pore-forming agent. The physicochemical properties, such as thermal stability, electrochemical working window, ionic conductivity, interfacial stability and surface morphology of the polymer electrolyte membranes, and the battery performance are investigated. And the results indicate that urea can be an excellent pore-forming agent to fabricate the polymer electrolyte membrane for the lithium ion battery.

2. Experimental

2.1. Preparation of GPEs

The P(VDF-HFP)-based polymer electrolyte membranes were prepared by the standard solution-casting technique in this work. The materials used were P(VDF-HFP) (Atofina, Kynar Flex, 12 wt.% HFP) and 1.0 M LiPF₆-ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethylmethyl carbonate (EMC) (1:1:1, v/v/v, Dongguan Shanshan Battery Materials Co., Ltd.). Prior to use, P(VDF-HFP) was dried under vacuum at 60 °C for 24 h. Urea and N,N-dimethylformamide (DMF) (A.R., Sinopharm Chemical Reagent Co., Ltd.) were used as pore-forming agent and solvent, respectively. Urea and P(VDF-HFP) mixture with different weight ratios, namely 0:4, 0.4:4, 0.6:4 and 0.8:4, were added accordingly and dissolved in DMF. The mixed solution was continuously stirred at 40 °C to obtain homogeneous casting solution, and then the solution was cast onto a glass plate with a doctor blade to form the wet membrane, the dry and porous membrane with the thickness about 120 μm was obtained by phase inversion technique after being dried in a vacuum oven at 120 °C for 10–12 h. The desired polymer electrolytes were achieved by being soaked the as-prepared circular polymer electrolyte membranes (18 mm × 0.12 mm) into the 1.0 M EC/DMC/EMC liquid electrolytes solution at room temperature for 1 h in the argon-filled glove box. For the sake of convenience, the as-prepared GPEs are labeled as N-x, in which x represents the adding amount of urea in the polymer electrolyte system.

2.2. Properties characterizations

The morphology and microstructure of P(VDF-HFP)-based polymer electrolyte membranes with different contents of urea were examined using a scanning electron microscope (SEM, JEOL JSM6301F). The X-ray diffraction (XRD, Rint-2000, Rigaku) using CuK α radiation ($\lambda = 0.15406$ nm) in the range of $2\theta = 5\text{--}60^\circ$ was employed to identify the crystalline phase of the as-prepared polymer electrolyte membranes. Fourier transform infrared (FT-IR) spectra were used to confirm the structure of the as-prepared GPEs on Nicolet 6700 instrument with a wave-number resolution of 2 cm^{-1} in the frequency of $4000\text{--}400\text{ cm}^{-1}$. Thermogravimetry and differential scanning calorimeter (TG-DSC) measurements of the polymer electrolyte membranes were carried out on a Perkin-Elmer Pyris-1 analyzer with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from 20 to 400 °C. A flow of argon gas was maintained over the perforated pan to avoid any contact with atmospheric moisture. The ionic conductivity of the blocking stainless steel (SS)/As-prepared electrolytes/SS model cells was determined at various temperatures (293–363 K, the cells were thermostated during measurements) by electrochemical impedance spectroscopy (EIS, CHI660b) with Ac amplitude of 10 mV from 10^5 to 0.01 Hz. Electrochemical working window of the Li/As-prepared electrolytes/SS asymmetrical cell was measured by running linear sweep voltammetry (LSV). The LSV tests were carried out using the same system as that in EIS at a scanning rate of 5 mV s^{-1} from 2.0 to 6.8 V. In addition, the interfacial properties between the electrolyte and the electrodes were studied by investigating the resistance change of the Li/As-prepared electrolytes/Li symmetrical cell at 30 °C with different storage times. The charge-discharge tests of the Li/GPEs/LiCoO₂ 2032 coin cells were carried out using Land Battery Test System (Wuhan Land Electronic Co., Ltd. China). The electrode formulation consisted of 80 wt.% LiCoO₂ (Dongguan Shanshan Battery Materials Co., Ltd.), 10 wt.% carbon black, and 10 wt.% PVDF. The charge-discharge cycling was performed at different current densities with cut-off voltages of 2.75–4.25 V at room temperature.

3. Results and discussion

3.1. Surface morphology

SEM images of different polymer electrolyte membranes are shown in Fig. 1. It is obviously observed that the surface morphology varies with various contents of added urea. Compared with pure P(VDF-HFP) membrane displayed in Fig. 1(A), the membranes with urea have more interconnected micro-pores, which suggests that the membranes can entrap more liquid electrolytes and provide more Li⁺ transferring passageways, and hence may show higher ionic conductivity. When the membranes are subjected to vacuum drying, the added urea begins to decompose into ammonia gas and carbon dioxide and then form micro-pores in the membranes. It is obviously observed from Fig. 1 that the amount of the micro-pores in polymer electrolyte membrane becomes more with increasing the added amount of urea, however the variation trend of the pore-size is much different, in which the pore-size firstly reaches a maximum and then decreases in the same condition. It is generally known that only abundant micro-pores with appropriate pore-size can entrap more liquid electrolytes without weakening the mechanical properties of the polymer electrolytes. Obviously, the polymer electrolyte membrane with 0.6 g urea presents the smoothest surface and most abundant micro-pores with appropriate pore-size, which may lead to the highest ionic conductivity and best interfacial stability.

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