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Effect of different contents of organic-inorganic hybrid particles poly(methyl methacrylate)–ZrO_2 on the properties of poly(vinylidene fluoride-hexafluoroprolene)-based composite gel polymer electrolytes

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ABSTRACT

Poly(vinylidene fluoride-hexafluoroprolene) (P(VDF-HFP))-based composite polymer electrolyte (CPE) membranes doped with organic-inorganic hybrid particles poly(methyl methacrylate)–ZrO_2 (PMMA-ZrO_2) are fabricated by phase inversion, in which PMMA is firstly successfully grafted onto the surface of the homemade nano-ZrO_2 particles via *in situ* polymerization confirmed by FT-IR. XRD and DSC patterns show that adding PMMA-ZrO_2 into the polymer matrix can decrease the crystallinity of the CPE membranes and TG curves indicate the CPE membranes possess desirable thermal stability. It can be found that the CPE membrane presents a uniform surface with abundant interconnected micro-pores when the added amount of PMMA-ZrO_2 increases to 5 *wt* % *vs.* polymer matrix, in which the ionic conductivity at room temperature and tensile strength can be up to 3.595 $mS\ cm^{-1}$ and 26.18 MPa, respectively. In particular, the CPE membrane shows the minimum deformation of about 8% after being exposed at 160 °C for 1 h, and the electrochemical working window of the assembled Li/CPE/SS cell can be stable at 5.1 V (*vs* Li/Li^+) at room temperature. Moreover, the $LiCoO_2$/CPE/Li coin cell can deliver a specific capacity of 114.5 $mAh\ g^{-1}$ with 79.13% capacity retention at 2.0 *C* after 110 cycles. The results suggest that the as-fabricated P(VDF-HFP)-based CPE doped with 5 *wt* % organic-inorganic hybrid particles PMMA-ZrO_2 can be a promising polymer electrolyte for lithium ion batteries.

1. Introduction

With the explosive development of energy storage devices, the lithium ion battery has been extensively applied in the fields of mobile phones, laptops, electric bicycles and cars. However, explosion and combustion accidents have been frequently reported due to the leakage of the traditional liquid electrolytes, which would leave serious potential safety hazards to the practical applications [1–3]. In recent years, much attention has been focused on the gel polymer electrolytes (GPEs), which possess excellent properties in terms of the improved thermal safety, high flexibility and non-leakage compared to the traditional liquid electrolytes [4–7]. However, GPEs are difficult to achieve practical applications due to their low ionic conductivity at room temperature, poor mechanical strength and inferior electrochemical properties [8–10]. Poly(vinylidene fluoride-hexafluoroprolene) (P(VDF-HFP)) has been extensively considered as a polymer matrix to prepare GPE membranes because it possesses an excellent chemical stability and mechanical plasticity. In addition, nano-sized inorganic fillers such as SiO_2 [11,12], TiO_2 [13,14], and Al_2O_3 [15,16] have been widely employed to modify and fabricate the composite polymer electrolytes (CPEs) to improve the mechanical properties and ionic conductivity of the battery system. Compared to the other inorganic particles, ZrO_2 can be selected as additive due to its great chemical-resistance and thermal stability. Wei X et al. [17] have prepared a high performance composite separator based on ZrO_2 nanoparticles, which exhibits high porosity and ideal electrochemical performances in comparison to the commercial polyolefin-based separator. However, ZrO_2 nanoparticles are very difficult to disperse into the polymer matrix, which would hinder the formation of the abundant porous structure of the CPE membrane. Recently, incorporating organic-inorganic hybrid particles into the polymer matrix has been proved to be conductive to

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overcome the drawbacks [18–20]. Poly(methyl methacrylate) (PMMA) is a typical amorphous polymer with several advantages of good dimensional stability and excellent flexibility [21,22]. Cao et al. [23] have reported that a nano-crystalline TiO_2-PMMA hybrid can be well dispersed into the P(VDF-HFP) matrix and the as-fabricated CPE presents excellent electrochemical properties. In the present work, organic-inorganic hybrid particles PMMA-ZrO_2 are synthesized via *in situ* polymerization, which are designed and employed to improve the dispersibility of nano-particles in the P(VDF-HFP) polymer matrix. And the CPE membranes doped with different amounts of hybrid particles PMMA-ZrO_2 are prepared by phase inversion, in which the physicochemical and electrochemical properties of the as-fabricated CPEs are investigated in detail.

2. Experimental

2.1. Synthesis of the hybrid particles PMMA-ZrO_2

Nano-ZrO_2 particles are prepared by hydrolysis of zirconium (IV) *n*-butoxide (80 *wt* %) in the mixture of *n*-butanol ($\geq$99.5 *wt* %) and deionized water. Firstly, 3.5 mL zirconium (IV) *n*-butoxide is mixed with 50 mL *n*-butanol to prepare the solution A, and 0.5 mL deionized water is added into another 50 mL *n*-butanol to prepare the solution B. Then the solution A and solution B are mixed together with vigorous stirring to hydrolyze and prepare zirconia sol at 60 °C for 20 h in the atmosphere of nitrogen. A fraction of ZrO_2 sol is further washed by sonication and centrifugation to remove excess solvent, and then the homemade nano-ZrO_2 particles can be obtained by being dried at 80 °C for 24 h. The other fraction of ZrO_2 sol is directly modified by vinyltrimethoxy silane (A171) to prepare the modified zirconia sol, in which the mass fraction of the silane in the ZrO_2 sol is about 3.5%. And then 5.0 mL methyl methacrylate (MMA, >99.5 *wt* %) as monomer and 0.05 g benzoyl peroxide as initiator (>98.0 *wt* %) are added into the modified sol simultaneously at 80 °C. After being stirred continuously for 4 h, the desirable PMMA-ZrO_2 hybrid particles can be obtained by being centrifuged, washed with ethanol, and then dried at 80 °C in vacuum for 24 h. All the reagents are purchased from Sinopharm Chemical Reagent Co., Ltd. with analytically pure and used as received without further purification.

2.2. Preparation of the CPEs

A certain amount of the as-prepared PMMA-ZrO_2 hybrid particles and P(VDF-HFP) (provided by Atofina, Kynarflex, 12 *wt* % HFP) are simultaneously added into *N*,*N*-dimethylformamide (purchased from Macklin Biochemical Co., Ltd.) to form a homogeneous coating solution by stirring at 40 °C for 2 h, where a weight fraction of PMMA-ZrO_2/P(VDF-HFP) can be fixed at 0, 3, 5 and 8%. After then, the homogeneous casting solution is cast onto the precleaned glass substrate with a doctor blade to fabricate the wet membranes. Then, the polymer electrolyte membranes are dried for 24 h at 60 °C to remove the residual solvent and then cut into a disk with a diameter about 16 mm. The desirable polymer electrolytes can be obtained after the as-prepared circular polymer electrolyte membranes (16 mm × 0.12 mm) are transferred into an argon-filled glove box and soaked with 1.0 M $LiPF_6$-EC/DMC/EMC liquid electrolytes solution (1:1:1, *v*/*v*/*v*, purchased from Dongguan Shanshan Battery Materials Co., Ltd.) for 0.5 h, which are marked as CPE-x ($x = 0$, 3, 5 and 8 *wt* %) for convenience. In addition, the P(VDF-HFP)-based polymer electrolyte doped with the homemade nano-ZrO_2 powders is also prepared for comparison by the same process, which is named as CPE-ZrO_2.

2.3. Properties characterization

The FT-IR spectra of the as-synthesized homemade ZrO_2, silane modified ZrO_2 and PMMA-ZrO_2 hybrid particles are recorded with a Nicolet iS50 Fourier transform infrared spectrometer in the wavenumber of 4000–400 cm^{-1}, and the size distribution of the homemade ZrO_2 particles is measured by the Malvern Zetasizer Nano S90. X-ray diffraction (XRD) patterns of the CPE membranes and nano-ZrO_2 particles are investigated on the Rint-2000, Rigaku, using Cu K_α radiation in the 2θ range of 10–60°. The morphology of the upper and lower surface of the as-prepared CPE membranes is examined by scanning electron microscope (SEM, JEOL, JSM6301F). The thermal analysis is performed by a Perkin-Elmer Pyris-1 analyzer with a heating rate of 10 °C min^{-1} from 50 to 400 °C in an argon atmosphere. The liquid uptake ratio (A) can be calculated using the following Eq. (1), in which w_0 is the weight of the dry piece, w_1 is the weight of the one after being fully swelled and A represents the liquid uptake ratio. The mechanical tensile strength (T) of the CPE membranes is tested with an electronic universal testing machine (Instron 5500) at a crosshead speed of 100 mm min^{-1}, using a rectangular shape (150 mm × 25 mm × 0.12 mm) at room temperature. The ionic conductivity of the stainless steel (SS)/CPE/SS simulated cells can be measured by electrochemical impedance spectroscopy (EIS) on the CHI660E analyzer (Shanghai Chenhua, China) in the frequency range from 10^5 to 1 Hz. The ionic conductivity (σ) of each polymer electrolyte can be calculated in accordance with the following Eq. (2), where R is the bulk resistance of the symmetrical cell, l and S are the thickness and the area of the specimen, respectively.

$$A\% = \frac{w_1 - w_0}{w_0} \times 100\% \tag{1}$$

$$\sigma = {}^{l}\!/_{(R\cdot S)} \tag{2}$$

The electrochemical working window can be determined by linear sweep voltammetry (LSV) using the same system as that in EIS with a scanning rate of 5 mV s^{-1} from 2.5 to 6.5 V at room temperature using the Li/CPE/SS simulated cell. The interfacial properties between the CPEs and the electrodes are investigated by monitoring the resistance change of the Li/CPEs/Li simulated cells at room temperature with different storage times. The battery performance with the as-prepared CPEs is evaluated by galvanostatic charge-discharge using the 2032-type coin cell, which is constructed with a lithium anode, a CPE, and a $LiCoO_2$ cathode. The charge-discharge cycling performance is investigated on Land Battery Test System (Wuhan Land Electronic Co., Ltd.) at different current densities (0.1, 0.2, 0.5, 1.0 and 2.0 *C*) with cut-off voltages of 2.75–4.25 V at room temperature.

3. Results and discussion

FT-IR spectrum of the homemade ZrO_2, silane modified ZrO_2 and PMMA-ZrO_2 hybrid particles are compared and displayed in Fig. 1. It can be obviously observed that the absorption bands demonstrated in Fig. 1(a) appear around at 496 cm^{-1} assigned to the stretching vibration of the –Zr–O– bonds from the nano-ZrO_2 powders and the peaks get weak shown in Fig. 1(b) and (c) due to the surface modification of the homemade nano-ZrO_2 powders. With the presence of vinyltrimethoxy silane, it can be observed from Fig. 1(b) and (c) that the –C=C- bonds can be distinctly detected around at 1601 cm^{-1}. Furthermore, the peaks appearing around at 1409 and 2951 cm^{-1} demonstrated in Fig. 1(b) and (c) can be assigned to the symmetrical and asymmetrical stretching vibrations of the –C–H– bonds from the methyl and methylene groups. Compared with the