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Preparation of core–shell structural single ionic conductor $SiO_2@Li^+$ and its application in PVDF–HFP-based composite polymer electrolyte

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ABSTRACT

Core–shell structural single ionic conductor $SiO_2@Li^+$ was successfully synthesized from vinyltriethoxysilane, sodium *p*-styrenesulfonate and $LiOH{\cdot}H_2O$ by hydrolysis, polymerization and ion exchange and confirmed by TEM and FT-IR. The poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF–HFP)-based composite polymer electrolyte (CPE) membrane doped with $SiO_2@Li^+$ was prepared by phase inversion method and the desirable CPE was obtained after being activated in liquid electrolyte. The physicochemical properties of the CPE were characterized by SEM, XRD, TG, and electrochemical measurements. The results show that the CPE membrane presents uniform surface with abundant interconnected micropores and possesses excellent mechanical performance with high decomposition temperature about 450 °C; and adding $SiO_2@Li^+$ into matrix remarkably decreases the crystallinity but enhances ionic conductivity of the CPE membrane; the ionic conductivity and lithium ion transference number at room temperature are up to 3.885 mS cm^{-1} and 0.4374, respectively, and the reciprocal temperature dependence of ionic conductivity of as-prepared CPEs follows Vogel–Tamman–Fulcher relation. The battery properties of the assembled cells using CPE doped with $SiO_2@Li^+$ as electrolyte show excellent rate and cycle performance, which is partly attributed to the improved interfacial performance between the electrolyte and electrodes and partly to enhanced electrochemical working window and lithium ion transference number.

1. Introduction

Gel polymer electrolytes (GPEs) have been considered as the most promising practical electrolyte of lithium ion battery for their excellent properties, such as flexible configuration and improved safety [1,2]. GPEs are mainly composed of plasticized polymer matrix and suitable organic additives, in which the entrapped liquid electrolyte can provide free lithium ions and the additives enhance battery performance [3,4]. However, due to the softening effect by liquid electrolyte, the inferior mechanical performance of polymer matrix prevents GPEs from practical applications [1]. Many efforts, such as selecting suitable matrix and incorporating inorganic filler into matrix, have been carried out to improve both the mechanical performance and ionic conductivity [3,5]. A copolymer of vinylidene fluoride and hexafluoropropylene (PVDF–HFP) is considered to be the most potential matrix as separator material, because it has relatively lower crystallinity due to the copolymerization effect between VDF and HFP in comparison with poly (vinylidene fluoride) (PVDF). In addition, HFP amorphous phase facilitates fast ionic conduction and VDF crystalline phase acts as a mechanical support for the membrane [2,5,6]. The reported ionic conductivity of PVDF–HFP-based polymer electrolyte is up to 5.3 mS cm^{-1} [5]. To further improve the ionic conductivity and mechanical properties of the GPEs simultaneously, adding inorganic nano-particles, such as silica (SiO_2), alumina (Al_2O_3), zirconia (ZrO_2), titania (TiO_2) and molecule sieves, into polymer matrix has also been proved to be a feasible approach [7–11]. Lithium ion transference number is also a key factor for lithium ion battery, because high lithium ion transference number can improve rate and cycle performance by increasing carrier number and lowering polarization. Therefore, adding suitable fast or single ionic conductor, such as $Li_{0.1}Ca_{0.9}TiO_3$, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ and polymer single ionic salt, into polymer matrix is a new idea to enhance the integrated performance of the battery [7,12–14]. In this work, the core–shell structural single ionic conductor $SiO_2@Li^+$ was synthesized via hydrolysis, polymerization and ion exchange, and the correspondingly desirable CPEs containing $SiO_2@Li^+$ were prepared by traditional phase inversion method. Physicochemical performance of the as-prepared CPEs is investigated by SEM, XRD, TG, electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV), the compatibilities between the electrolyte and the $LiCoO_2$ and graphite electrodes are also studied by battery tests. And the results prove that the as-prepared CPE doped with $SiO_2@Li^+$ presents excellent practical applications.

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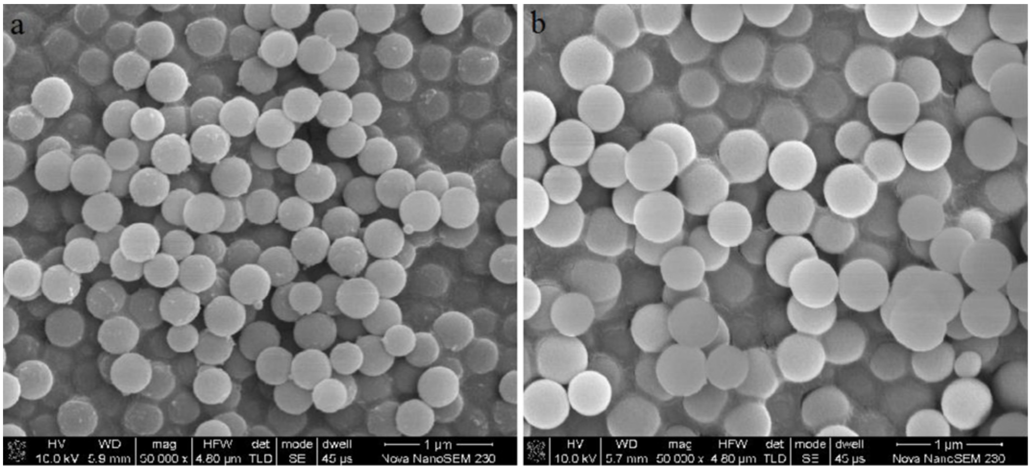

Fig. 1. FE-SEM images of nano-SiO_2 and SiO_2@Li^+ powder.

2. Experimental

2.1. Materials

PVDF–HFP (Atofina, Kynar Flex, 12 wt.% HFP) was used as polymer matrix and analytical reagent vinyltriethoxysilane (VTES, Sinopharm Chemical Reagent Co., Ltd.) was employed to provide silica source. Sodium *p*-styrenesulfonate (Adamas Reagent Co., Ltd.) and $LiOH{\cdot}H_2O$ (Sinopharm Chemical Reagent Co., Ltd.) were used as received without further purification.

2.2. Preparation of SiO_2@Li^+

The core–shell structural SiO_2@Li^+ was synthesized via hydrolysis, polymerization and ion exchange. At first, the spherical nano-SiO_2 was prepared from the mixtures of VTES and absolute alcohol in the presence of ammonia according to hydrolysis described by Stober [15]. Then the intermediate SiO_2@Na^+ can be attained by the polymerization between the nano-SiO_2 and sodium *p*-styrenesulfonate using azobisisobutyronitrile (AIBN) as an initiator at 60 °C for 8 h. And the white powder SiO_2@Li^+ can be obtained from the SiO_2@Na^+ and $LiOH{\cdot}H_2O$ via ion exchange at 90 °C for 12 h after drying under vacuum at 80 °C for 10 h [13,16].

2.3. Preparation of CPEs doped with SiO_2@Li^+

The CPEs doped with SiO_2@Li^+ were fabricated by standard solution-casting technique coupled with traditional phase inversion method. Appropriate amount of as-prepared SiO_2@Li^+ and PVDF–HFP were added into N,N-dimethylformamide to form homogeneous casting solution with continuous vigorous stirring for 4 h at 40 °C, in which the weight ratio of SiO_2@Li^+ to PVDF–HFP was kept 1:10. The resulting solution was cast onto Teflon plate with a doctor blade to form the wet membrane after leaving still for 1 h at 40 °C, and then the wet free-standing membrane with Teflon plate was immersed into a coagulation bath for 12 h at room temperature. Finally, the resulting free-standing CPE membrane with a thickness about 120–150 μm was obtained by drying under vacuum at 60 °C for 24 h to remove the residual solvents and then transferred into an argon-filled glove box for storage. In order to attain CPEs, the as-prepared membranes were cut into a disk with a diameter about 18 mm and immersed into 1.0 M $LiPF_6$-ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethylmethyl carbonate (EMC) (1:1:1, w/w/w) liquid electrolyte solution (Dongguan Shanshan Battery Materials Co., Ltd.) at room temperature for 1 h to activate. Meanwhile, the PVDF–HFP-based composite polymer electrolytes modified with as-prepared nano-SiO_2 was also prepared as control samples in this work.

2.4. Properties characterization

The surface morphology of as-prepared nano-SiO_2 and SiO_2@Li^+ powder was observed with field emission scanning electron microscopy (FE-SEM, SIRION 200) and the surface and cross-section morphology and pore size of the CPE membranes was evaluated by scanning electron microscope (SEM, JEOL JSM6301F). And the

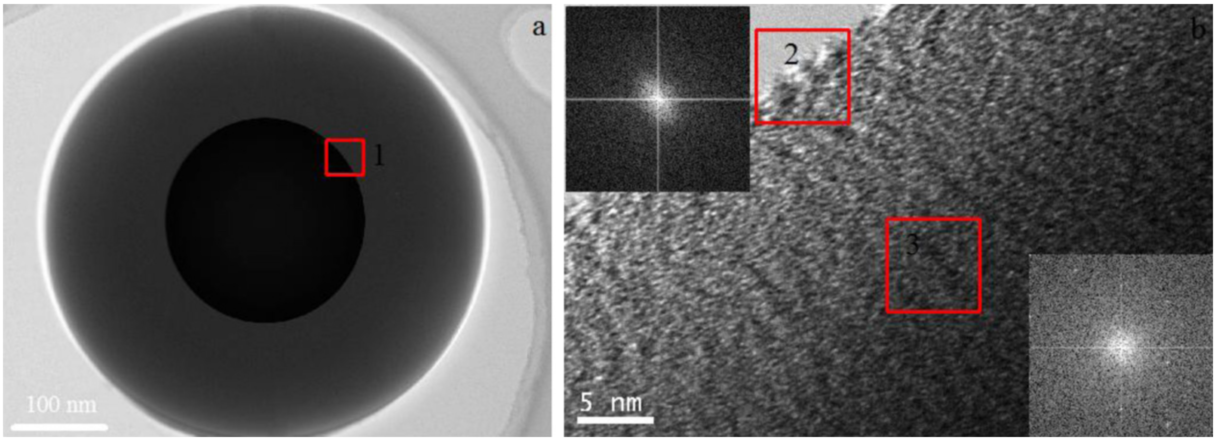

Fig. 2. (a) TEM image of core–shell structural SiO_2@Li^+ powder; (b) HRTEM image of the selected area 1 in (a) and Fourier transform of the selected area 2 and 3.