



Porous polymer electrolytes with high ionic conductivity and good mechanical property for rechargeable batteries



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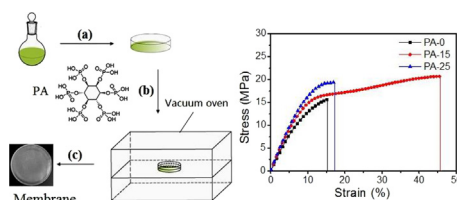
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HIGHLIGHTS

- A porous polymer electrolytes (PPEs) doped with phytic acid (PA) is prepared.
- PA improves the mechanical properties of the PPEs as a crosslinker and plasticizer.
- The PPEs demonstrate compatible mechanical properties and conductivity.

GRAPHICAL ABSTRACT



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ABSTRACT

Porous polymer electrolytes (PPEs) are attractive for developing lithium-ion batteries because of the combined advantages of liquid and solid polymer electrolytes. In the present study, a new porous polymer membrane doped with phytic acid (PA) is prepared, which is used as a crosslinker in polymer electrolyte matrix and can also plasticize porous polymer electrolyte membranes, changing them into soft tough flexible materials. A PEO–PMMA–LiClO₄–x wt.% PA (x = weight of PA/weight of polymer, PEO: poly(ethylene oxide); PMMA: poly(methyl methacrylate)) polymer membrane is prepared by a simple evaporation method. The effects of the ratio of PA to PEO–PMMA on the properties of the porous membrane, including morphology, porous structure, and mechanical property, are systematically studied. PA improves the porous structure and mechanical properties of polymer membrane. The maximum tensile strength and elongation of the porous polymer membranes are 20.71 MPa and 45.7% at 15 wt.% PA, respectively. Moreover, the PPEs with 15 wt.% PA has a conductivity of 1.59×10^{-5} S/cm at 20 °C, a good electrochemical window (>5 V), and a low interfacial resistance. The results demonstrate the compatibility of the mechanical properties and conductivity of the PPEs, indicating that PPEs have good application prospects for lithium-ion batteries.

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1. Introduction

With the rapid development of portable electronic devices and electric vehicles, lithium-ion batteries (LIBs) with high energy density, good charge/discharge rate, and high safety have attracted

substantial attention as promising energy storage devices [1–5]. As one of the critical elements of such devices, polymer electrolyte plays a key role in the electrochemical properties of batteries. Among all kinds of polymer electrolytes, porous polymer electrolytes (PPEs), in which liquid electrolyte is immobilized in a polymer matrix, have been attractive for use in developing LIBs because of the combined advantages of liquid electrolyte (high ionic conductivity) and solid polymer electrolyte (good mechanical property) [6–8]. The performance of PPEs prepared by immersing porous

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membranes into liquid electrolyte depends mainly on the porous structure [9,10]. Therefore, preparing a polymer membrane with an optimized porous structure is highly important.

Generally, porous membrane materials were prepared through Bellcore technique [11], phase inversion process [7,12,13], and direct evaporation technique [14–16]. The Bellcore technique has been widely used in preparing a porous polymer membrane based on poly(vinylidene fluoride)-co-hexafluoropropene (PVDF-HFP), which has good ionic conductivity at room temperature after soaking with liquid electrolyte [11]. However, the process of dibutyl phthalate (DBP) extraction requires large volumes of organic solvents, which increases the production costs, and the removal of DBP is not 100% efficient. Gerbaldi et al. prepared an innovative V_2O_5 -based multiphase electrode/electrolyte composite by UV-induced free-radical photo-polymerization [17]. The polymer electrolyte has an open structure on its surface, which can easily allow the infiltration of the liquid electrolyte. Compared with the Bellcore technique, the phase inversion process has main advantages such as simple procedures and environmentally friendly features [18,19]. Xiao et al. reported a novel PPE based on PVDF/PEO-*b*-PMMA (PEO: poly(ethylene oxide); PMMA: poly(methyl methacrylate) blends that were prepared by the phase inversion technique, in which a PEO-*b*-PMMA block copolymer could obviously improve the porous structure [7].

However, high porosity usually leads to the decrease of tensile strength. The maximum stress of pure PVDF membrane is 5.93 MPa, while that of PVDF/PEO-*b*-PMMA PPEs drops to 4.25 MPa. Nevertheless, the elongation of PVDF/PEO-*b*-PMMA PPEs (18.48%) is larger than that of pure PVDF membrane (8.59%) by 9.89%. Wang et al. prepared PPEs by gelating the liquid phase in the pores of the PVDF membrane with a low molecular weight organogelator and 1,3:2,4-di-O-methylbenzylidene-D-sorbitol (MDBS) [8]. The mechanical property is sacrificed to obtain sufficient conductivity when the amount of MDBS is increased. The tensile strength and Young's modulus of the pure PVDF membrane were 7.1 MPa and 194 MPa, respectively. However, the tensile strength and Young's modulus of the PPEs without MDBS were 5.8 MPa and 46.6 MPa, respectively. For the case of PPEs with MDBS, the tensile strength and Young's modulus were lower than those of PPEs without MDBS. Zhai et al. demonstrated that adding ionic liquids (ILs) [BMIM]BF₄ improved the ionic conductivity and stability of electrode/polymer electrolyte (E/P) interface [20]. Unfortunately, the mechanical property of PPEs decreased. Xing et al. synthesized the mesoporous PVDF piezo-separator by using ZnO nanowire (NW) arrays as a template. They demonstrated that the porous structure of a PVDF separator can facilitate the transportation of Li⁺, resulting in higher energy-storage efficiency [21]. Kim et al. fabricated a piezoelectric β -form PVDF separator with a highly porous architecture by introducing ZnO particles [22]. The lower charge-transfer resistance of this well-developed porous piezo-separator is the main factor that facilitated the transport of Li⁺ without sacrificing the piezoelectric performance. Zalewska et al. investigated the effect of ILs and surface-modified inorganic filler addition on the properties of polymer electrolytes [23]. The addition of Al₂O₃ led to a threefold decrease in E/P interface resistance, which stabilized at 1500 Ω . Moreover, the mechanical property of the polymer electrolyte membrane increased. Nevertheless, the pore structure of the polymer electrolyte membrane was not good and the inorganic filler in the polymer electrolyte membrane could be aggregated. The mechanical property of PPEs is often sacrificed to obtain sufficient conductivity, which hinders the commercialization of LIBs on a large scale.

Cross-linking is an effective way to suppress crystallization and is also beneficial in enhancing the tensile strength of the polymer [24–26]. As an environmentally friendly, biocompatible, nontoxic,

inexpensive, and abundant organic acid, PA is extensively used in biosensor, nanomaterial, cation exchange resin, anticorrosion, and other fields because of its special inositol hexaphosphate structure shown in Fig. 1d [27–29]. PA is a major component of all plant seeds, constituting 1%–3% of the weight of many cereals and oil-seeds and typically accounting for 60%–90% of total phosphorus [30]. Jiang et al. prepared novel proton-conducting polymer electrolyte membranes from bacterial cellulose (BC) by incorporating PA for fuel cells [28]. The breaking strength of BC membranes weakened as the low concentration of PA increased and the elongation remained unchanged. With the rise of PA concentration, the breaking strength decreased rapidly, while the elongation increased and the yielding phenomenon became more remarkable. The results suggested that PA could also plasticize BC membranes, changing them into soft tough flexible materials. PA was used as both the gelator and dopant to react with the aniline monomer by protonating the nitrogen groups on polyaniline (PANI), leading to the formation of a three-dimensional (3D) interconnected network structure [31,32]. In the present study, PA was introduced into the polymer electrolyte for LIBs, which may improve the mechanical properties and the formation of porous structure. PEO-based polymer electrolytes have been extensively studied because of the ability to form complexes with a variety of lithium salts [33–36]. PMMA has good compatibility with the liquid component entrapped in the matrix [20,37]. Meanwhile, the properties of the blended PEO–PMMA polymers can be easily controlled by changing the composition [38]. Furthermore, PEO and PMMA have good compatibility [12,39–41]. Lithium perchlorate (LiClO₄) has a smaller ionic radius and dissociation energy and is highly soluble in most organic solvents [42,43].

In this study, the PEO–PMMA–LiClO₄-*x* wt.% PA (*x* = weight of PA/weight of polymer) polymer membrane was prepared through the evaporation method. The effects of the ratio of PA to PEO–PMMA on the properties of the porous membrane, such as morphology, porous structure, and mechanical property, as well as the thermal and electrochemical properties of the PPEs are systematically studied.

2. Experimental section

2.1. Preparation of porous polymer membranes

The mixture of 0.4 g PMMA(AR, $M_w = 550,000$, Alfa Aesar), 0.1 g PEO (AR, $M_w = 300,000$, Aladdin), and 0.025 g LiClO₄ (99.9%, Aladdin) was dissolved in 12 ml N-methyl-2-pyrrolidone (AR, Tianjin Kermel Chemical Reagent Co. Ltd.), which was stirred for 12 h at 40 °C until the homogeneous solutions were obtained. The *x* wt.% (*x* = 0, 5, 10, 15, 20, 25) of PA (50 wt.%, Aladdin) was added to the solution, which was stirred for 1 h and the ultrasonic dispersed for 30 min at 40 °C. The solution was cast on a Petri dish, covered by perforated paper, and allowed to evaporate in a vacuum oven at 90 °C for 24 h. The membranes were then dried in a vacuum oven at -0.08 MPa, 90 °C for 12 h, in which the solvent was removed completely. From the vacuum oven, the membranes were transferred to a dry box and immersed in 1 M LiPF₆ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC; 1:1:1 by volume; Shenzhen CAPCHEM Technology, China) to make the PPEs.

2.2. Characterization

The microstructure of the polymer matrix was characterized with field emission scanning electron microscopy (SEM) (JSM 6360LV). The Fourier transform infrared (FTIR) spectra of the prepared polymer matrices were recorded using a Nicolet 6700

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