



A sodium ion conducting gel polymer electrolyte



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ABSTRACT

A sodium ion conducting gel polymer electrolyte based on poly(vinylidene difluoride-co-hexafluoropropylene) porous membrane is reported, which is prepared through a simple phase separation process. It exhibits high safety, good mechanical properties and good electrochemical stability. The gel polymer electrolyte provides the sodium ionic conductivity of 0.60 mS cm^{-1} at ambient temperature, while the commercial separator (Celgard 2730) offers only 0.16 mS cm^{-1} . The temperature dependence of the ionic conductivity from 25 to 75 °C is consistent with an Arrhenius-behavior. The ionic transference number of sodium ion (t_{Na}^+) in the gel polymer electrolyte is 0.30, higher than that (0.17) in the commercial separator. This provides a new direction to improve the safety of sodium ion batteries.

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1. Introduction

Clean and renewable energy sources are urgently needed because of air pollution, emissions of climate-warming gases from the burning of fossil fuels and the slow depletion of the world's supply of fossil fuels, and the recent concern about energy conversion and storage systems is growing to meet the increasing demand for use of the intermittent renewable energy sources from such as wind, solar and waves. Lithium ion batteries have captured the portable electronics market owing to its high voltage and high energy density [1–6]. However, with the widespread use of lithium ion batteries thus rapidly growing demand for lithium commodity chemicals, lithium supply might limit the application of lithium ion batteries in large scale energy storage systems.

Sodium is the most promising alternative to lithium for energy storage applications based on its high abundance, low cost, and suitable redox potential ($E_{\text{Na}^+/\text{Na}}^0 = -2.71 \text{ V}$ vs. standard hydrogen electrode; 0.3 V above that of lithium). In spite of the little lower output voltage and lower energy density of sodium ion batteries compared with those of lithium ion batteries, the abundance and lower cost of raw materials are more critical in large scale energy storage systems where the weight requirement is less severe [7,8].

High temperature Na/S and Na/NiCl₂ cells have been tried for applications in energy storage system. However, to maintain the sodium in liquid state, they are operated at elevated temperatures (300–350 °C) where complicated materials and technologies are needed to ensure

their durability and safety [9]. Thus there has been increasing interest to the non-aqueous, ambient temperature sodium ion batteries [10–20].

Similar to lithium ion batteries, sodium ion batteries require essential safety precautions considering the existence of organic liquid electrolytes which are easy to catch on fire sometimes leading to explosion during misuse [21,22]. The use of solid electrolytes to replace the organic electrolyte can be a solution to improve the safety and avoid liquid leakage. Considering the low ionic conductivity ($<10^{-4} \text{ S cm}^{-1}$) and poor mechanical strength of the solid electrolytes [23], gel polymer electrolytes (GPEs), which have unique hybrid structures combining polymer with liquid electrolyte and thus possess cohesive properties of solids and diffusive properties of liquids simultaneously, have received increasing attention due to their good ionic conductivity, wide electrochemical window, good compatibility with electrodes and good thermal stability [24–33].

By virtue of its attractive properties, poly(vinylidene difluoride), PVDF, has been chosen as a polymer host for lithium ion battery applications [34]. PVDF-based GPEs are highly electrochemically stable due to the presence of a strong electron-withdrawing functional group (–C–F). Furthermore, poly(vinylidene difluoride-co-hexafluoropropylene), P(VDF-HFP), is a semi-crystalline polymer with a significantly reduced degree of crystallinity due to the addition of hexafluoropropylene (HFP) unit [35]. Therefore, it shows high flexibility as compared to PVDF [36] and a dielectric constant of 8.4, which favors the larger dissolution of lithium salts and subsequent support of a high concentration of charge carriers.

Some composite polymer electrolytes for sodium ion have been prepared by such as template imprinting, but the preparation condition is very tedious due to critical moisture control [37]. The well-known Bellcore technique for lithium ion gel polymer electrolytes is based on an extraction process [38]. However, the extraction process needs a

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large quantity of organic solvent which is impractical for large scale application. Besides, it is hard to remove the plasticizer completely by extracting and drying, which would lead to a poor electrochemical behavior.

Here we used a simple phase separation process to prepare a highly porous polymer membrane based on P(VDF-HFP) for sodium ion conducting gel polymer electrolyte. Using water acting as the non-solvent and pore inducer instead of the extraction step requiring volatile solvents, it is of great promise from the point of view of economy and environmental friendliness for practical application.

2. Experimental section

2.1. Preparation of the porous polymer membrane

The preparation of the porous P(VDF-HFP) membrane is based on our former reported method [39]. P(VDF-HFP) was dissolved into a mixture of *N,N*-dimethyl formamide (DMF) and distilled water with a weight ratio of P(VDF-HFP):DMF:H₂O = 15:85:3. The solution was cast onto a clean glass plate, and then immersed in a water bath at 80 °C, yielding a homogeneous white membrane, which was dried under vacuum at 100 °C for 10 h. The dried pieces were soaked in an organic electrolyte (1 M NaClO₄ or LiClO₄ solution in EC/DMC/DEC (ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate), 1/1/1, w/w/w, Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd) over 12 h in a glove box (water content: <1 ppm) to obtain the gel polymer electrolyte (GPE) for further electrochemical measurement.

2.2. Physical characterization

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the membranes were carried out by utilizing a PerkinElmer TGA7/DSC7, with a heating rate of 10 °C min⁻¹.

The surface morphology of the prepared membranes was investigated by a Philips XL30 scan electron microscopy (SEM). The membranes were dipped into liquid nitrogen and broken into two parts, and then SEM micrographs of the cross-sections were taken. All of the samples were sputtered with gold prior to the SEM measurement.

Porosity (*P*) was calculated from Eq. (1):

$$P = \frac{100(W_s - W_0)}{\rho_b V_0} \% \quad (1)$$

where *W*₀ and *W*_s are the weights of the membranes before and after the absorption of the *n*-butyl alcohol, respectively, ρ_b is the density of *n*-butyl alcohol, and *V*₀ is the apparent volume of the membrane.

The amount of liquid electrolyte uptake (ΔW) was calculated from Eq. (2):

$$\Delta W = \frac{100(W_s - W_0)}{W_0} \% \quad (2)$$

where *W*₀ and *W*_s are the weights of the membranes before and after the absorption of the organic electrolyte, respectively.

A stress-strain test was conducted using a Shanghai Sans YG832 tensile testing machine with a crosshead speed of 2 mm min⁻¹ according to Standard GB/T 13022-91 plastics-determination of tensile properties of films. The width and length of the sample were 4 mm and 15 mm, respectively.

2.3. Electrochemical measurements

The ionic conductivities were measured by electrochemical impedance spectroscopy (EIS). In blocking type cells, the GPE membranes saturated with the liquid electrolytes were sandwiched between two stainless steel (SS) electrodes. As for the non-blocking type cells, the

GPE membranes were sandwiched between two sodium or lithium metal electrodes. Impedance data were obtained with an electrochemical working station CHI660C (Chenhua) in the frequency range 10 Hz–100 kHz between 25 and 75 °C. The ionic conductivity (σ) was calculated from Eq. (3):

$$\sigma = \frac{d}{R_b \cdot S} \quad (3)$$

where *R*_b is the bulk resistance; *d* is the thickness of the polymer electrolyte, and *S* is the area of the stainless steel electrode.

The total number of ion transference was calculated based on Eq. (4):

$$t_{ion} = \frac{I_t - I_e}{I_t} \quad (4)$$

where *I*_t and *I*_e are the total and residual currents, respectively.

The cation (i.e., sodium ion) transference numbers of the gel polymer electrolyte films were estimated using a combination of a.c. impedance and d.c. polarization techniques [40]. It was obtained by the electrochemical working station measuring in blocking-type cells where the GPE membranes were sandwiched between two sodium metal electrodes. The step potential was 10 mV. The value of *t*_{Na⁺} was calculated from Eq. (5):

$$t_{Na^+} = \frac{I_s(\Delta V - R_0 I_0)}{I_0(\Delta V - R_s I_s)} \quad (5)$$

where *I*₀ and *I*_s are the initial and final currents, respectively, and *R*₀ and *R*_s are the cell resistances before and after the polarization, respectively.

The Na₄Mn₉O₁₈ cathode was prepared by mixing 80 wt.% Na₄Mn₉O₁₈ powder, 10 wt.% carbon black and 10 wt.% polyvinylidene difluoride (PVDF) dissolved in *N*-methyl-2-pyrrolidone (NMP) to form slurry. Then, the electrode slurry was pasted on Al foil and dried. Cyclic voltammetry was performed with the Na₄Mn₉O₁₈ cathode and Na metal as the counter and reference electrodes, respectively, at 25 °C under a scan rate of 0.1 mV s⁻¹. The electrolyte was the gel polymer electrolytes or Celgard 2730 saturated with the NaClO₄ electrolyte. Cyclic voltammetry was also performed on the symmetric cells: Na/GPE/Na and SS/GPE/SS (stainless steel), at 25 °C at a scan rate of 1 mV s⁻¹.

3. Results and discussion

The surface and cross-section morphology of the porous polymer membrane is shown in Fig. 1. There are pores with a diameter range of 1–2 μm on the surface (Fig. 1a, b), whose structure is similar to those of the traditional separators. Between the surface and bottom layers there is a porous structure with well-organized interconnecting cellular pores with the diameter of about 1.5 μm (Fig. 1c). It is clear that the added liquid electrolyte can be entrapped in the pores of the polymer matrix, preventing the leakage of the absorbed liquid electrolyte. The porosity was determined to be 61%, which is almost within the range of most separators, 40–60%. Its uptake for the liquid electrolyte is up to 112 wt.%, which is enough to provide high ionic conductivity.

Poor mechanical strength might limit the application of gel polymer electrolytes in large-scale systems. The well-organized cellular pores could be helpful to maintain the framework of the polymer matrix. As shown in Fig. S1 of the Supporting Information, the tensile strength and breakage elongation of the porous P(VDF-HFP) membrane are 7.6 MPa and 148%, respectively, which is acceptable for the manufacturing of sodium ion batteries.

Thermal stability is also an important issue for the application of gel polymer electrolytes in sodium ion batteries. As shown in Fig. S2 of the Supporting Information, the porous P(VDF-HFP) membrane is thermally stable up to 130 °C (near to its melting point), which is almost the

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