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$Na_{3.4}Zr_{1.8}Mg_{0.2}Si_2PO_{12}$ filled poly(ethylene oxide)/$Na(CF_3SO_2)_2N$ as flexible composite polymer electrolyte for solid-state sodium batteries

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HIGHLIGHTS

- NASICON filler affects the conductivity mechanism in PEO/NaTFSI polymer electrolytes.
- NASICON-PEO/NaTFSI composite polymer electrolyte exhibits high conductivity.
- Solid-state battery employing this electrolyte shows excellent cycling performance.

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ABSTRACT

Solid electrolytes with high ionic conductivity and excellent electrochemical stability are of prime significance to enable the application of solid-state batteries in energy storage and conversion. In this study, solid composite polymer electrolytes (CPEs) based on sodium bis(trifluorosulfonyl) imide (NaTFSI) and poly (ethylene oxide) (PEO) incorporated with active ceramic filler (NASICON) are reported for the first time. With the addition of NASICON fillers, the thermal stability and electrochemical stability of the CPEs are improved. A high conductivity of 2.8 mS/cm (at 80 °C) is readily achieved when the content of the NASICON filler in the composite polymer reaches 50 wt%. Furthermore, $Na_3V_2(PO_4)_3$/CPE/Na solid-state batteries using this composite electrolyte display good rate and excellent cycle performance.

1. Introduction

Due to the huge abundance and low cost of sodium resources, sodium ion batteries are considered to be an alternative in the large-scale energy storage field [1–3]. The increasing demand in pursuit for batteries with enhanced safety and higher energy density has spurred an upsurge in the research interest in the solid polymer electrolytes (SPEs) as substitution for the conventional liquid electrolytes. Compared to their liquid counterparts, these SPEs possess many advantages, including no leakage, suitable for flexible battery design, and wider working temperature. Owing to these merits, solid polymer electrolytes have been extensively studied in the field of portable devices and large-scale energy storage applications, such as electric vehicles. Poly (ethylene oxide) (PEO) was firstly proposed to be an alternative polymer host matrix, which can dissolve Li/Na salts to form polymeric electrolytes and allow ion transport in the amorphous area [4].

However, PEO based electrolytes exhibit low ionic conductivity (10^{-8}-10^{-7} S/cm) because of the high crystallinity of PEO at room temperature [5,6]. Several possible strategies have been proposed to improve the ionic conductivity *via* suppressing crystallization: polymer blending [7–10], crosslinking [11,12], as well as the addition of inorganic fillers (e.g., Al_2O_3, TiO_2, ZrO_2, SiO_2) [13–17] to form ceramic polymer electrolytes (CPEs). The inorganic fillers contribute to increase the ionic conductivity in two aspects [18]: (1) suppressing the local crystallization behavior of the polymer matrix and therefore increasing the mobility of chains; (2) providing more ion conducting pathways at the surface regions of the fillers. In addition, the incorporation of the fillers is supposed to improve the stability at the interface between the electrolyte and electrodes [19–26]. The ceramic fillers can be divided into two types: inactive fillers (e.g., TiO_2, Al_2O_3) [14–17] and active fillers or fast ion conductors which can provide active sites for ion conduction (e.g., $Li_{0.33}La_{0.557}TiO_3$, $Li_7La_3Zr_2O_{12}$, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$) [27–29]. Compared with inactive fillers, the incorporation of active fillers generally leads to higher conductivity and higher mobile ion transference number since the active fillers participate in the conduction process of mobile ions [29].

The anions of salts also have significant effects on the conductivity of the polymer electrolytes. Up to now, amongest a variety of salts that

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have been studied as conducting salts for the PEO-based polymer electrolytes [30–35], $TFSI^-$ based salts show the best conductivity [36,37]. This is mainly attributed to the large size and flexibility of $-SO_2-N-SO_2^-$ anion, which are beneficial to reduce the crystallinity of PEO matrix and result in plasticizing properties [38,39]. Moreover, the high degree of charge delocalization of $TFSI^-$ leads to much weaker ion-ion interactions, thus increases the dissociation and solubility of $TFSI^-$ in PEO matrix [40,41].

Recently, Na ion hybrid electrolytes [42–44] were reported to exhibit good electrochemical properties. However, safety issues still exist because of the liquid electrolyte contained in these hybrid electrolytes. In this contribution, a fast ion conductor, NASICON structured $Na_{3.4}Zr_{1.8}Mg_{0.2}Si_2PO_{12}$, was incorporated into NaTFSI-PEO_{14} to form a solvent-free composite polymer electrolyte (CPE) for the first time. The relationship between the ratio of the NASICON filler and the ionic conductivity of the CPE is extensively investigated. A high ionic conductivity of 2.8 mS/cm at 80 °C can be achieved when 50 wt% NASICON filler is contained. The electrochemical window and thermal stability of the CPEs are evaluated. In addition, the reasons for the enhancement in the ionic conductivity are also discussed. With this CPE as the separator and electrolyte, the solid-state $Na_3V_2(PO_4)_3$/CPE/Na battery exhibits good rate capability and cycle performance. These CPEs are promising solid electrolytes for the development of all-solid-state batteries.

2. Experimental

Electrolyte preparation. The NASICON electrolyte was synthesized through sol-gel method as described in our previous work [45,46].

PEO polymer (Aldrich; Mw 600,000) was dried under vacuum at 50 °C for 24 h. Sodium bis(trifluoromethanesulfonylimide) [$Na(CF_3SO_2)_2N$, NaTFSI] (Aldrich) were dried under vacuum at 60 °C for 24 h. The composite polymer electrolytes were prepared by dissolving appropriate amount of PEO and NaTFSI (with a O: Na = 14 in molar ratio) in anhydrous acetonitrile. After stirring for 24 h, NASICON powder was added and the solution was mixed by a ball milling for 12 h. The obtained slurry was then casted on to a finely-polished Teflon plate. After slow evaporation of the solvent at room temperature, the cast films (200-300 μm thick) were dried under high vacuum for 24 h at 60 °C to eliminate any solvent residuals. The sample preparation was performed in a glove box under argon atmosphere ($[H_2O] < 0.1$ ppm, $[O_2] < 0.1$ ppm).

Cathode preparation and cell assembling. $Na_3V_2(PO_4)_3$ was prepared *via* a solid-state reaction according to a previous work [47]. A stoichiometric mixture of NaH_2PO_4 and V_2O_3 (Alfa Aesar, 99.4%) were ballmilled for 6 h and then dried in the oven. Afterwards, the precursors were sintered at 900 °C for 24 h under the Ar atmosphere.

The cathode was prepared by coating a slurry containing $Na_3V_2(PO_4)_3$, NASICON ceramic powder, Super P carbon and poly (vinylidene fluoride) (PVDF) binder (65: 20: 5: 10 by weight ratio) onto Al foil. The cathode film was cut into small pieces with an area of $0.64\ cm^2$ (0.8 cm × 0.8 cm) and dried under vacuum at 120 °C for 12 h.

Solid-state NVP/CPE/Na cells were assembled by sandwiching the composite polymer electrolyte between the sodium anode and the $Na_3V_2(PO_4)_3$ cathode. All the cells are assembled in an argon filled glove box ($[H_2O] < 0.1$ ppm, $[O_2] < 0.1$ ppm). After the cell assembling process, the cells were kept at 80 °C for 4 h before test, in order to obtain good interfacial contact between the electrolyte and electrodes.

Characterization. TGA and differential scanning calorimetry (DSC) traces were conducted on Netzsch STA 449C differential scanning calorimeter in Ar atmosphere at a scanning rate of 10 °C/min from room temperature to 250 °C.

The linear sweep voltammetry (LSV) test was conducted on a Na/CPE/Na cell with a stainless steel as working electrode and sodium foil as counter electrode under 70 °C. The scanning rate was 0.1 mV/s over a range of 2.5–5.0 V *vs.* Na^+/Na.

The cross-sectional morphology of the composite polymer electrolyte was observed using a scanning electron microscope (Hitachi S-4800). The elemental distribution on the cross-sectional area of the composite polymer electrolyte was collected by energy dispersive X-ray spectroscopy (EDX).

Ionic conductivity measurements were performed using an impedance analyzer (Im6e) in the frequency range of 100 mHz-8 MHz. The CPE films were cut to discs and sandwiched between two blocking stainless steel electrodes. The cells were kept at 70 °C for 2 h in order to guarantee a good electrolyte-electrode contact and then conserved at room temperature for 10 days before test. Thereafter, the impedance spectra were collected from 20 °C to 100 °C with an equilibration time of 8 h for each test. The ionic conductivity (σ) can be calculated according to the formula:

$$\sigma = R/(L\cdot S)$$

where R is the resistance of the electrolyte, and can be obtained from the Nyquist plot, L is the thickness of electrolyte, S is the contact area between the electrolyte and the electrodes.

The charge/discharge tests of the cells were performed at current rates of 0.1C, 0.2C and 0.5C in a voltage range of 2.5 V and 3.8 V under 80 °C.

3. Results and discussion

NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, $0 \le x \le 3$) structured ceramic electrolytes have been widely studied because of their high ionic conductivity, thermal stability and wide electrochemical window [46,48,49]. By introducing Mg into the NASICON system, the ionic conductivity can be improved, which has been demonstrated in our previous work [45]. The ionic conductivity of $Na_{3.4}Zr_{1.8}Mg_{0.2}Si_2PO_{12}$ (NZMSPO) determined from a dense ceramic disk is 1.6 mS/cm at 25 °C [45]. In this study, NZMSPO (still labeled as NASICON) was used as ceramic filler in the PEO_{14}-NaTFSI polymer electrolyte.

The cross-sectional SEM images of the 50 wt%NASICON-NaTFSI-PEO_{14} CPE (labeled as 50 wt%NASICON-CPE) are displayed in Fig. 1(a) and Fig. 1(b). The average thickness of the composite polymer electrolytes is 200–300 μm, as shown in Fig. 1(a). Fig. 1(b) shows that the NASICON ceramic fillers with a particle size ranging from 500 nm to 2 μm distribute homogenously in the PEO matrix. It can be noticed that the NASICON particles can form continuous and interconnected junction when the content of the filler reaches 50 wt%. The elemental distributions of the Zr, Na, C, F in the electrolyte are characterized by the EDX mapping. As shown in Fig. 1(c), the F element from the NaTFSI salt and the C element from the PEO are evenly distributed, suggesting that the NaTFSI salt is well dissolved in the PEO matrix. It can also be seen that the Na and Zr elements arising from the NASICON ceramic filler are uniformly embedded in the PEO matrix.

TGA was employed to examine the thermal stability of polymer electrolytes. The decomposition behaviors of filler free SPE and 50 wt% NASICON-CPE are shown in Fig. 2(a). For both electrolytes, no mass loss occurs below 100 °C, indicating that both electrolytes are solvent-free. The weight loss at 237.5 °C for the filler free SPE is ascribed to the decomposition of PEO, while no weight loss occurred for the 50 wt% NASICON CPE up to 250 °C. This implies that the incorporation of NASICON filler suppresses the decomposition of PEO and improves the thermal stability compared to filler free SPE. Fig. 2(b) displays the DSC curves of the polymer electrolytes. The exothermic peaks detected in the DSC curves correspond to the melting temperature (T_m) of each component and equal to the crystallization temperature (T_c) of the PEO matrix. With the increase in the content of the NASICON filler, the exothermic peak broadens and shifts towards lower temperature. Therefore, the addition of NASICON filler lowers the crystallinity of PEO and increases the amorphous extent of PEO matrix simultaneously,