

An investigation of poly(ethylene oxide)/saponite-based composite electrolytes

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Abstract

Two kinds of composite, based on poly(ethylene oxide) (PEO) and a mineral saponite, were prepared and their thermal behavior, phase composition, microstructure and electrical properties were investigated. The results showed that PEO easily intercalates to the interlayer of saponite, replaces the interlayer water molecules, and acts as medium for lithium ions conduction. PEO-intercalated saponite exhibited conductivity as high as $4.1 \times 10^{-3} \text{ S cm}^{-1}$, a lithium ion transference number of 0.99 at 25 °C and conductivity activation energy of 0.14 eV. Appropriate amounts of intercalated PEO in the interlayer of saponite is important to an ideal ionic conductivity. The PEO-intercalated saponite is thermally stable below 350 °C. In addition, a PEO-based composite with lithium saponite as filler showed a homogeneous morphology and combined properties of individual PEO and saponite. The PEO-intercalated saponite could be considered as a good candidate as filler for lithium conductive polymer electrolyte.

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1. Introduction

Because of safety, high power and energy density reasons, fully solid state lithium batteries based on dry polymer electrolyte in conjunction with lithium anode and moderate voltage cathodes such as vanadate, sulphide, etc. have attracted new interest in the scientific and industrial communities. Poly(ethylene oxide) (PEO)/lithium salt-based polymer electrolytes have been adopted most frequently in such lithium batteries. Ionic conductivity, lithium ion transference number, mechanical strength and so on are the main research topics for the PEO-based polymer electrolytes. The combination of PEO and nanosized ceramic powders such as TiO_2 , SiO_2 , $\gamma\text{-LiAlO}_2$, BaTiO_3 , etc. has been demonstrated as one of the most favorable routes to improve the overall properties of the polymer electrolytes [1–4]. It has demonstrated that the addition of these previously mentioned ceramic fillers improves very effectively the conductivity of PEO-based electrolyte as well as its interfacial behavior with the lithium electrode. In addition to the ceramic fillers mentioned

previously, some minerals such as montmorillonite, laponite, etc. have also been reported to be very promising fillers for PEO-based polymer electrolytes [5–8]. The effects of fillers in the PEO-based electrolytes on the improvement of ionic conductivity might be attributed to an enhanced degree of amorphicity of the PEO chains with hindered recrystallization. In this work, we present a series of composite electrolytes in which PEO or a mineral acts as matrix. We chose saponite, a mineral compound with much higher ionic conductivity than montmorillonite [9]. We will pay particular attention to intercalation of PEO molecules to the interlayer of saponite to replace its water molecules. The ionic conductivity and lithium ion transference number of the composite electrolytes is also investigated.

2. Experimental

In this work, we prepared two kinds of combinatorial PEO and saponite materials. One is denominated as PEO-intercalated saponite, for which the water molecules in the interlayer of saponite will be replaced by PEO molecules. Another kind, denominated as PEO/saponite composite, is a PEO-based composite with saponite as filler.

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Synthetic saponite (Mineral Compound Institute, China) with average particle size of 20–30 nm was first treated with aqueous solution of LiOH until all conductive Na⁺ ions were exchanged by Li⁺ ions. Atomic absorption spectroscopy analysis showed that no obvious sodium was observed after 1-week treatment for the samples obtained. To prepare PEO-intercalated saponite, the lithium saponite obtained was then treated to replace its interlayer water molecules by dispersing saponite powders in the acetonitrile solution of PEO (MW = 2 × 10⁵) at 50 °C with gentle magnetic stirring for 1, 2 and 5 h, respectively, then properly washed the intercalated samples with acetonitrile solvent and dried them at 90 °C for 1 week.

In order to prepare PEO/saponite composite, given amounts of PEO and saponite are mixed homogeneously in an agate mortar inside an argon gas filled glove box. The mixture of PEO and the lithium saponite is then immediately heated at 90 °C for 1 week. Melting and crystallization of the composite electrolytes were evaluated by a DSC experiment carried out with Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 5 °C min⁻¹.

Phase analysis of the precursor saponite and the exchanged samples was carried out by using an X-ray diffractometer with Cu K α radiation (Rigaku RAX-10). Microstructure of composite was observed on a scanning electron microscope of model EPMA-8705QH₂ with the samples sputter-coated with gold.

The ac impedance plots were made to measure the ionic conductivity of composite samples by using stainless steel electrodes on a Solartron 1260 frequency response analyzer with an amplitude of 10 mV. The data were collected over a frequency range from 1 Hz to 1 MHz and a temperature range of 25–100 °C. Samples for conductivity measurements were prepared by isostatically pressing the composite polymer electrolytes into discs under a certain pressure. The pressed samples were sandwiched between two stainless steel electrodes under a pressure induced by a spring inside the test container. In order to satisfy interface contact between the solid electrolyte and stainless steel electrodes, all samples sandwiched were first kept at 80 °C overnight and then cooled down to room temperature and kept for several days at ambient temperature. At each test temperature, the samples were kept at least for 1 h to attain thermal equilibration.

Lithium ion transference number of the composite electrolytes was obtained by using cells with symmetrical non-blocking lithium metal electrodes according to the method reported by Bruce et al. [10,11] and calculated by the following equation:

$$t_{\text{Li}^+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

where ΔV is a dc polarization applied to the cell; I_0 and I_s are the initial and steady state currents during the polarization, respectively; and R_0 and R_s the resistance of the cell

determined by ac impedance analysis, before and after the dc polarization process, respectively.

3. Results and discussion

3.1. Thermal behavior

Fig. 1 shows typical DSC traces of the precursor saponite, the lithium-exchanged saponite, and its PEO-intercalated saponite as well as the PEO/saponite composite. It is shown that the precursor and the lithium-exchanged saponite have similar thermal behavior, with strong endothermic peaks at 120 and 135 °C, respectively, corresponding to the decomposition of the adsorption and the interlayer water of the saponites.

PEO containing systems presented different thermal behaviors. For the freshly prepared PEO-intercalated saponite, all samples showed similar DSC traces, regardless of the intercalation period. It can be found from Fig. 1 that no thermal effects were found below 350 °C, the exothermic band around 420 °C would be ascribed to the decomposition of PEO in the interlayer of saponite. After keeping at ambient temperature for 1 week, no obvious change in the DSC traces could be found. It is noteworthy that the melting point of crystalline PEO at about 65 °C has not been observed in the PEO-intercalated saponites, even if the samples were kept at low temperature for a long period. Therefore, the PEO residing in the interlayer of saponite is in amorphous state and kept stable within a long period.

The PEO/saponite composite shows combinatorial thermal behavior of pristine PEO and the PEO-intercalated saponite, with a strong endothermic effect at around 70 °C

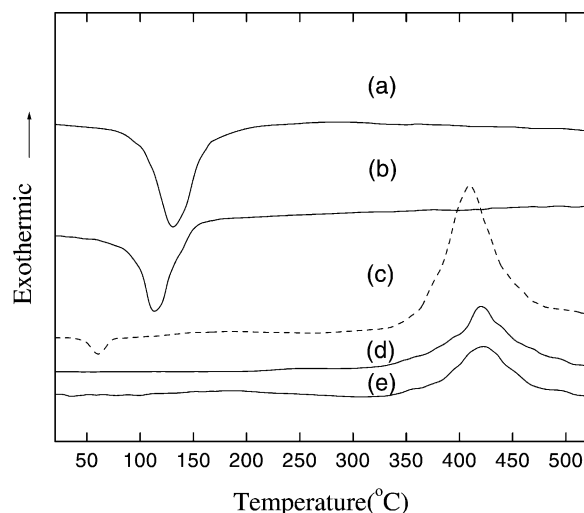


Fig. 1. DSC traces for various saponites: (a) lithium saponite; (b) precursor sodium saponite; (c) PEO/lithium saponite composite; (d) PEO-intercalated saponite kept at ambient temperature for 1 week; (e) freshly prepared PEO-intercalated saponite (2 h).

which is similar to the melting point of pristine PEO. In fact, the composite obtained at a higher temperature is a combined system of PEO-intercalated saponite and pristine PEO which enwraps the saponite particles in the composite.

3.2. Phase analysis

Fig. 2 shows X-ray diffraction (XRD) patterns of precursor lithium saponite, PEO-intercalated saponite and a PEO/saponite composite. It is obviously shown that the PEO-intercalated saponite has very similar XRD pattern to that of the precursor lithium saponite, which means that the replacement between water molecule and PEO molecule does not destroy the layered structure of saponite, but causes some diffraction peak shift to smaller angle side. The longer the intercalation time, the more the amount of PEO intercalated into the interlayer of saponite, therefore the bigger will be the 2θ shift. Table 1 lists the d value of (0 0 1) face for various saponites.

We have also measured the TEM image and its corresponding electron diffraction pattern for the PEO-intercalated lithium saponite treated for different times. The experimental results show that the crystalline feature of the original saponite particles remained with average particle size of 20–25 nm. No strong agglomeration of the saponite particles is observed. Fig. 3a and b shows the typical microstructure of PEO/saponite containing 5 and 50 wt.% of saponite, respectively, and it can be observed that the saponite particles are nearly homogeneously dispersed in PEO matrix.

As shown in Fig. 2, the PEO/saponite composite shows evidently a combination of diffraction peaks of both the saponite and PEO phases.

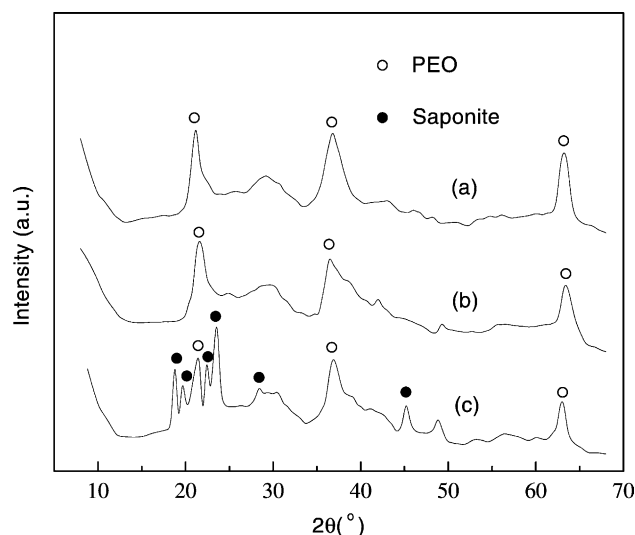


Fig. 2. Typical X-ray diffraction patterns for: (a) lithium saponite; (b) PEO-intercalated lithium saponite (2 h); (c) composite of 50PEO/50saponite.

Table 1

The d value of (0 0 1) face of various PEO-intercalated saponites

Sample	d (Å)
PEO-intercalated saponite (1 h)	15.51
PEO-intercalated saponite (2 h)	15.82
PEO-intercalated saponite (5 h)	16.13

3.3. Electrical properties

Impedance plots have been employed to evaluate the ionic conductivity and the corresponding activation energy for precursor saponites, PEO-intercalated saponite and PEO/saponite composite. It was found that all impedance spectra of lithium-exchanged saponite and its PEO-intercalated systems show a depressed semicircle and we therefore calculated the total electrical conductivity according to the intersection of the semicircle and the real axis of the plot. Fig. 4 illustrates the temperature dependence of the total conductivity for isopressed discs of PEO-intercalated lithium saponites of various intercalation times. For comparison, the temperature dependence of conductivity measured for a PEO/saponite composite is also included. It is clearly shown in the figure that all PEO-intercalated saponites behave linearly within the whole testing temperature range. And we can see that the conductivity of the PEO-intercalated saponite varies as a function of the content of PEO intercalated into the interlayer of saponite which is related to the intercalation time.

Table 2 summarizes the conductivities of pristine PEO polymer and PEO-intercalated saponite and their composite electrolytes. Their lithium ion transference number and conductivity activation energy are also listed together with their conductivities. As listed in the table, all PEO-intercalated saponites are nearly pure lithium ion conductors and exhibit higher conductivity than some other layered lithium-exchanged silicate minerals such as montmorillonite [12]. This is a similar case for interlayer water containing lithium saponite and montmorillonite, where the former has an ionic conductivity of $3.18 \times 10^{-3} \text{ S cm}^{-1}$ [9], about one order of magnitude higher than the latter. It is interesting to pay attention to the influence of the intercalated interlayer PEO content on the ionic conductivity of the materials. At first, the conductivity increases with the intercalation of PEO, then decreases with further PEO intercalation, as is listed in Table 2. So, the longer the intercalation time, the thicker will be the interlayer, and therefore the more the PEO content is in the layer. We could ascribe the decrease of conductivity to the deficiency of lithium ions in the interlayer when extra PEO is intercalated into the saponite. In comparison to ionic conductivity, the activation energy is less affected by the amount of intercalated PEO.

Up to now, PEO/LiN(CF₃SO₂)₂ is among the polymer electrolytes with highest ionic conductivity; however, its lithium ion transference number is very low, usually lower than 0.1, which means a relatively large contribution owes to the corresponding anions of the salt and would result in a

notable concentration polarization at the interface between the polymer electrolyte and an electrode. If the electrolyte is applied in an electrochemical device such as a lithium battery, the concentration polarization will cause serious degradation of cell capacity during charge–discharge cycling. The PEO-intercalated saponites show high lithium ion transference numbers in addition to high ionic conductivity, and should be potential candidates for additives of polymer electrolytes. Hereby, we tested the ionic conductivity of PEO/saponite composite. Unfortunately, they exhibited much lower conductivity than the iso-pressed PEO-intercalated saponite, which could be ascribed to a strong chemical

Table 2
Typical conductivities of saponite-based electrolytes at 25 °C

Sample	σ (S cm ⁻¹)	t_{Li^+}	E_a (eV)
Saponite (Na)	3.18×10^{-3}	–	–
Saponite (PEO) (1 h) ^a	2.1×10^{-3}	0.99	0.16
Saponite (PEO) (2 h) ^a	4.1×10^{-3}	0.99	0.14
Saponite (PEO) (5 h) ^a	1.5×10^{-3}	0.98	0.15
5 wt.% PEO/95 wt.% saponite ^b	1.4×10^{-3}	0.98	0.16
50 wt.% PEO/50 wt.% saponite ^b	6.3×10^{-5}	–	–
PEO	2×10^{-8}	–	–

^a PEO-intercalated saponite within various periods.

^b Composite of PEO and saponite prepared by melting process.

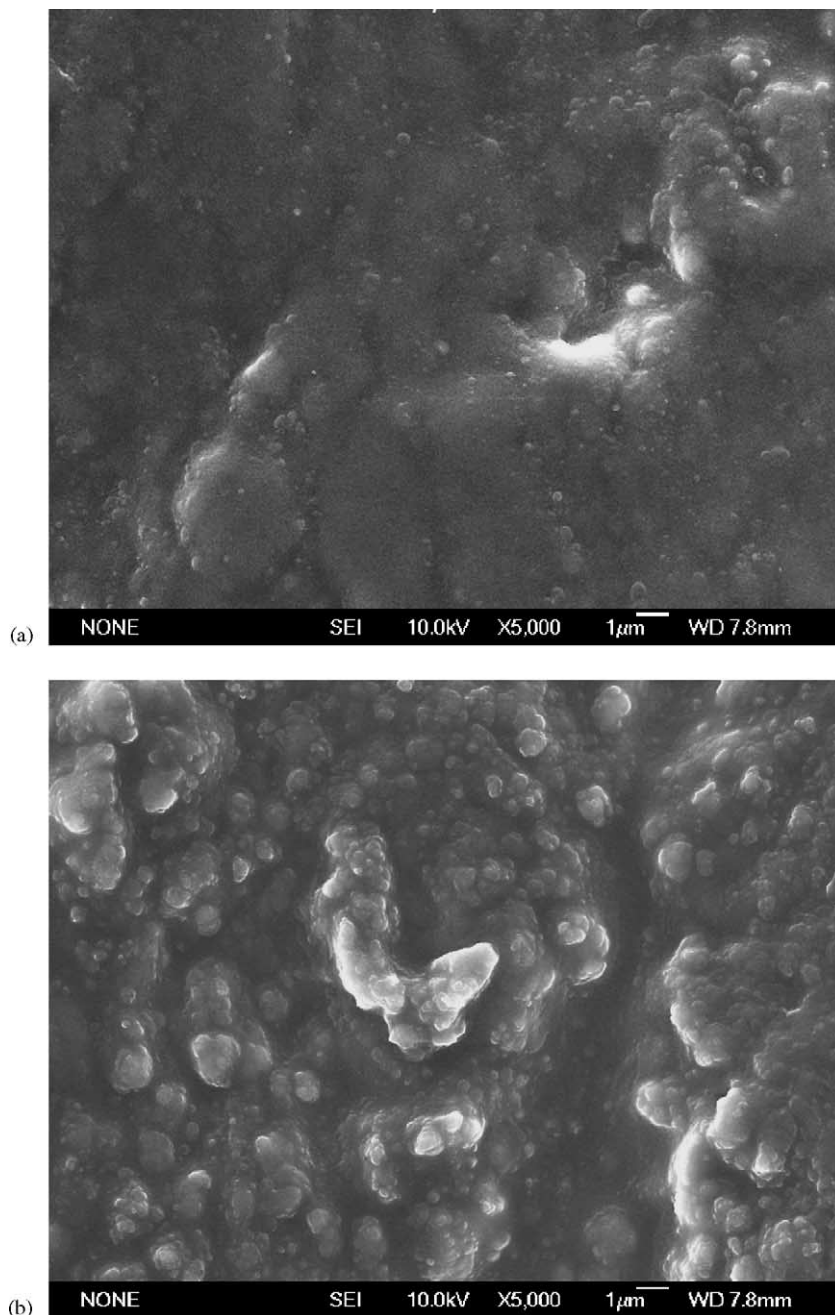


Fig. 3. Typical microstructure of PEO/saponite composite containing (a) 5 wt.% and (b) 50 wt.% saponite, respectively.

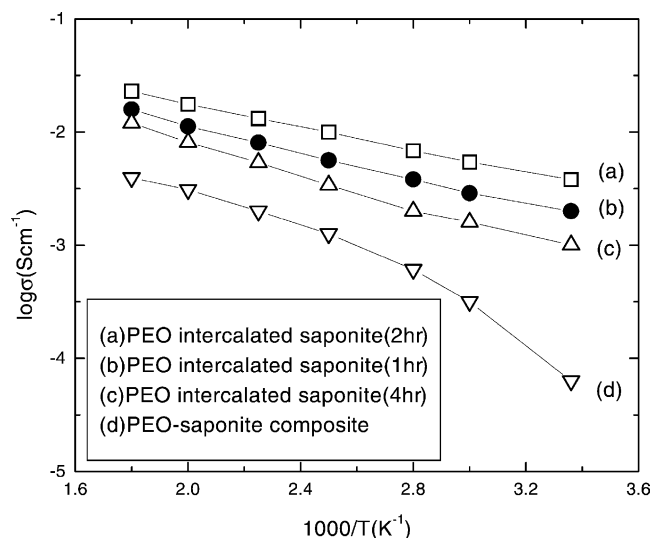


Fig. 4. Arrhenius plots of the conductivity of various PEO-intercalated saponites and PEO/saponite composites.

bond between the lithium ion and saponite matrices and the insolubility of lithium saponite in PEO matrix. Nevertheless, its value of conductivity is still higher than those of the composite electrolyte of PEO and montmorillonite [12].

4. Conclusions

PEO-intercalated lithium saponites exhibit excellent and pure lithium ion conduction behavior. The value of

the ionic conductivity depends on the content of PEO inside the interlayer of saponite, which is proportional to the intercalation time. An appropriate ratio of Li^+ to the PEO content in the interlayer is essential to improve the lithium ion conductivity. The PEO-intercalated saponites show crystalline structure similar to its precursor, and exhibits good thermal stability. Conclusively, PEO-intercalated saponites are promising candidate for a lithium ion conductor.

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