

# Structure and Properties of an Organic Rectorite/ Poly(methyl methacrylate) Nanocomposite Gel Polymer Electrolyte by *In Situ* Synthesis

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**ABSTRACT:** The synthesis of organic-modified rectorite (OREC)/polymethyl methacrylate (PMMA) nanocomposite gel polymer electrolyte (NGPE) via *in situ* polymerization was investigated using free radical initiator in an solution, in which organic plasticizer, propylene carbonate(PC) acted as a solvent. A series of NGPE membranes with different OREC content were prepared and characterized. The dispersion and exfoliation statuses of the OREC in the prepared NGPE membranes were analyzed through X-ray diffraction (XRD) and transmission electron microscope (TEM), and the results indicated that for the NGPE with 5 wt % OREC membrane, OREC was partly exfoliated and well dispersed in the gel polymer electrolyte system. The electrochemical properties of the NGPE were determined by alternating current (AC) impedance spectroscopy, which illustrated that the ionic conductivity of the nanocomposite gel polymer electrolyte firstly increased and

then decreased with increasing OREC content. Meanwhile, the maximum value of ionic conductivity for nanocomposite gel polymer electrolytes was obtained when organic clay amount was 5 wt %. The interactions among the components of the NGPE were investigated by Fourier transform infrared (FTIR) spectroscopy. It was shown that there were specific interactions between OREC and the other components, which may influence the conductivity and the stability of GPEs. Finally, an thermal stability enhancement was presented by NGPE with 5 wt % OREC compared with GPE, which was determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2632–2638, 2009

**Key words:** nanocomposite gel polymer electrolyte; ionic conductivity; thermal stability; lithium ion batteries

## INTRODUCTION

Polymer electrolytes have been widely developed for rechargeable lithium-ion batteries applications over the last few decades.<sup>1,2</sup> Among them, gel polymer electrolytes (GPEs) have received considerable attention because they combine the advantages of liquid electrolytes with high-ionic conductivity and solid electrolytes in terms of absence of leakage. Nevertheless, with the existence of organic solvent, GPEs still have some drawbacks such as thermal instability and poor mechanical properties. Recently, nanocomposite gel polymer electrolytes (NGPEs) have been found as its possessing excellent ion con-

ductivity and thermal stability compared with GPEs.<sup>3–5</sup> The ceramic fillers such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> can be added in GPEs to improve their properties.<sup>6,7</sup>

In comparison to the common inorganic ceramic powders, layered clays are the most appealing feature in terms of extreme enhancement on the mechanical and thermal stability with respect to polymer matrix due to its particular swollen layered structure. So far, montmorillonite (MMT) is one of the widely studied clay minerals, which was applied to modifying polymer matrix. Upto now, several profound investigations of interaction between the clay and different polymers have been already done. Chen and Chang<sup>8</sup> prepared NGPEs using MMT as filler and its shown excellent conductivity. Rectorite (REC) is another type of clay mineral, which presenting similar structural characteristics as MMT. It is a sort of regularly interstratified clay mineral with alternate pairs of dioctahedral mica-like layer (non-expansible) and dioctahedral smectite-like layer (expansible) in a 1:1 ratio. The Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> cations lie in the interlayer region of 2:1 mica-like

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layers and 2:1 smectite-like layers, whereas the exchangeable hydrated cations reside in the latter. The layer distance (d-spacing) of rectorite is enlarged after organic modification, thus organic-modified rectorite (OREC) shown excellent compatibility with polymer matrix.<sup>9</sup> Our previous research investigated that the insertion of well-dispersed OREC layers (intercalated or exfoliated) in the polymer matrix, such as thermoplastic polyurethane and polypropylene,<sup>10,11</sup> could bring the enhancement on both mechanical properties and thermal stabilities. According to Huang et al.<sup>12,13</sup> NGPE can be prepared through a simple procedure by blending OREC and PMMA directly. This procedure causes some disadvantages, such as how to remove of the residual solvent and the poor performance of the free standing membrane. Meanwhile, the relationship between the structure and properties of NGPE is rarely discussed.

In this study, an organic-modified rectorite/poly (methyl methacrylate) (OREC/PMMA) gel polymer electrolyte was synthesized through *in situ* polymerization with free radical initiator in the solution, in which organic plasticizer propylene carbonate (PC) acts as solvent of polymerization. Since organic plasticizer used here acts the solvent for both procedures of synthesis and casting, it avoids the procedure of removing the second solvent from the gel system. The structure and micromorphology of NGPE was investigated by X-ray diffraction (XRD) and transmission electron microscope (TEM). The electrical properties of the NGPE were determined by electrochemical impedance spectroscopy. The influence of the polymerization by adding OREC, and the reactions between the components in the NGPE were also observed. The thermal stability of the gel system was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The mechanism of the increase of conductivity of the OREC/PMMA gel electrolyte was explored on the basis of its structure-properties relationship.

## EXPERIMENTAL PROCEDURE

### Materials

Raw materials including methyl methacrylate (MMA) were provided by Sinopharm Chemical Reagent Beijing Co. (Beijing, China) and purified by distillation under reduced pressure at 35°C. Propylene carbonate (PC) was supplied by Sinopharm Chemical Reagent Co. (Shanghai, China) and used as received. Lithium perchlorate (LiClO<sub>4</sub>) was supplied by No.2 reagent factory of Shanghai (Shanghai, China) and vacuum dried at 120°C for 24 h. The free radical initiator, 2,2-azobis (isobutyronitrile) (AIBN), was purchased from Shanghai Sanpu Chemical Co. (Shanghai, China) and twice purified by recrystalli-

zation in methanol. Rectorite (REC) was refined from clay minerals available in Wuhan, Hubei province (Wuhan, China). OREC was prepared through the organic-modification method as follows.

A certain amount of the clay was suspended in deionized water in a glass vessel using a glass rod. The dodecyl benzyl dimethyl ammonium bromide was purchased from Shanghai, China and used as received. It was dissolved in a prescribed amount of water, and then added to the suspended clay-water solution, with vigorous stirring for several minutes at room temperature. The mixture was transferred to a three-neck flask, heated to 85°C, and under stirring for 5 h. The treated products were washed and filtered repeatedly to ensure the complete removal of bromide ions; the filtrate was titrated with AgNO<sub>3</sub> until AgBr precipitate was not observed. The products were then dried at 100°C for several hours to obtain designated OREC, with a d-spacing of 2.57 nm, which was evaluated by means of XRD.

### Synthesis of NGPE

OREC is well dispersed in PC through high-speed shear, from which we obtained a suspension called constituent I. Then dissolved the LiClO<sub>4</sub> in PC to gain liquid electrolyte as Constituent II. Adding MMA and AIBN together with the other two constituents in a flask. After the mixture was stirred in a water bath at 80°C for 3 h under a nitrogen atmosphere, the pre-electrolyte suspension has been already prepared for casting. The gel composition used for the electrolyte is given as 20/PMMA:73.5/PC:6.5/LiClO<sub>4</sub> by weight.

### Preparation of the NGPE membrane

The NGPE membrane was prepared by casting pre-electrolyte suspension on a Teflon plate. Then, the pre-electrolyte membrane was treated at 80°C for 8 h in oven that filled with nitrogen under standard atmosphere, forming a gel polymer electrolyte membrane. In this work, NGPE membranes with different OREC content (0, 1, 2, 3, 5, and 7 wt % based on gel polymer electrolyte) were prepared and investigated, respectively. The thickness of the membrane was in the range of 0.8–1.3 mm.

### Methods

Gel permeation chromatography (Waters, 150-C ALC/GPC) measurements were performed using tetrahydrofuran (THF) as solvent and applying a flow rate of 0.5 mL min<sup>-1</sup>.

Wide-angle XRD measurements were conducted with an X-ray automatic generator (D/max-3C, Rigaku, Tokyo, Japan). The X-ray beam was derived

from nickel-filtered Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation in a sealed tube operated at 40 kV and 40 mA. The XRD patterns were acquired at room temperature in the  $2\theta$  range of  $2^\circ$  to  $10^\circ$ .

The status of dispersion and layered structure of OREC in the gel system were inspected by a Hitachi H-800 transmission electron microscope (Osaka, Japan). Ultra-thin frozen sections were cut with a microtome and then were treated at  $80^\circ\text{C}$  for 8 h in vacuum oven to remove the plasticizer.

Fourier transform infrared (FTIR) absorption spectra were obtained with a WQF-31 spectrometer in the wave frequency range of 500 to  $4000\text{ cm}^{-1}$ .

The ionic conductivity of the sample was determined by the alternating current (AC) impedance analysis, which measured by an impedance analyzer (produced by Hioki, model 3532-50 LCR). The gel electrolyte membrane was placed between two stainless steel blocking electrodes in a cell apparatus. The alternating current frequency introduced in this study was from 42 Hz to 5 MHz. The electrode area was  $1.1\text{ cm}^2$ . The ionic conductivity was calculated by the following equation:

$$\sigma = L/(SR_b), \quad (1)$$

where  $L$  is the thickness of the membrane;  $S$  is the contact area between the electrode and the electrolyte membrane;  $R_b$  is the bulk impedance of the electrolyte membrane.

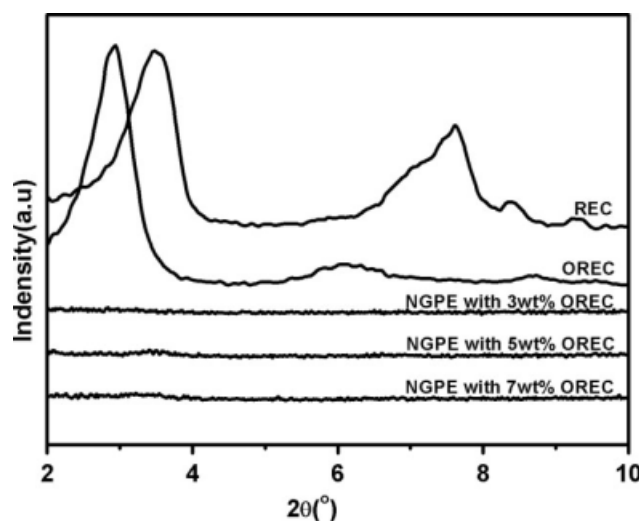
Differential scanning calorimetry (DSC) analysis was performed on a TA Instrument (model 2910 MDSC) from  $25$  to  $200^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . Thermogravimetry analysis (TGA) was conducted using a TGA apparatus (model SDT2960) from  $25$  to  $570^\circ\text{C}$  at a heating rate of  $20^\circ\text{C min}^{-1}$  under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

The average molecular weight ( $M_w$ ) of the pure PMMA prepared in PC was  $1,806,000\text{ g mol}^{-1}$ , with a narrow molecular-weight distribution ( $M_w/M_n = 1.06\text{--}1.07$ ). The gel polymer electrolyte (GPE) membrane without clay prepared in this work was colorless, free standing, and homogeneous, whereas the NGPE membranes are gray, free standing, and homogenous.

### XRD analysis

High-speed shear is an excellent method to facilitate delamination process and prepare the polymer/clay nanocomposite. In this work, OREC/PMMA suspensions were prepared through high-speed shear to achieve a NGPE with high-degree delamination. X-ray diffraction (XRD) patterns are shown to



**Figure 1** XRD patterns of REC (a), OREC (b), NGPE with 3 wt % OREC (c), NGPE with 5 wt % OREC (d), and NGPE with 7 wt % OREC (e).

characterize the exfoliation status of clay in nanocomposite gel electrolytes. Figure 1 shows the XRD patterns of unmodified REC, OREC, and OREC/PMMA NGPE with different OREC contents. The interlayer distances of natural and organic clay are 2.2 and 2.57 nm, respectively, which are calculated by Bragg's equation.<sup>11</sup> The enlarged interlayer distance indicates that sufficient cation exchange reaction was carried out through organic modification, which might facilitate excellent exfoliation of clay in the NGPEs. Moreover, the XRD patterns of the NGPEs with different OREC additions do not show any 001 peak in the  $2\theta$  range of  $2^\circ$  to  $10^\circ$ , demonstrating that the d-spacing of OREC layers is adequately enlarged after the *in situ* synthesis and the clay present exfoliated layers structure in the gel composite system.

### TEM analysis

TEM studies are necessary to verify the extent of exfoliation achieved besides XRD analysis. The micrograph of the NGPE with the 5 wt % addition of OREC is shown in Figure 2. The black lines represent the clay layers. It is clear that OREC platelets are uniformly dispersed throughout the gel polymer matrix, which means that OREC can be exfoliated as fine layers and dispersed randomly in NGPE when *in situ* polymerization was carried out with PC and lithium salt.

### FTIR spectra of OREC/PMMA

NGPE is a type of multiconstituents system, and intermolecular interaction is an important factor of



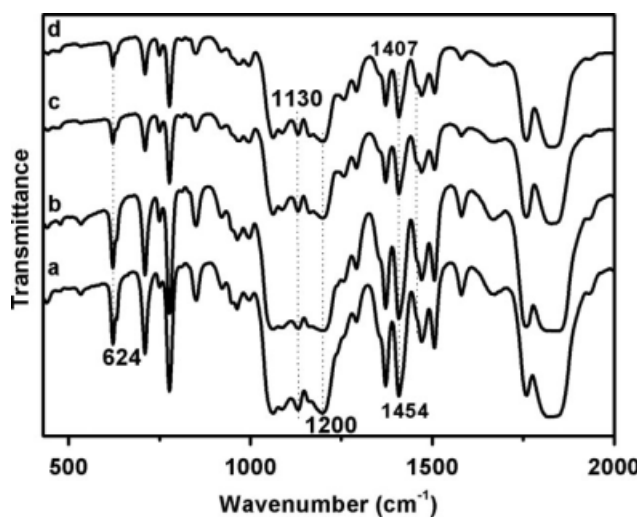


**Figure 2** TEM micrographs of NGPE with 5 wt % OREC. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

representation of structure modification. The interaction behavior was characterized and analyzed by FTIR spectra.

The FTIR spectra of pure PMMA and nanocomposite gel electrolytes containing 1, 3, and 5 wt % OREC are shown in Figure 3. In the spectra, the C=O symmetrical stretching of PMMA gives a peak at  $1730\text{ cm}^{-1}$ , asymmetric stretching vibrations of the C—O—C bond are exhibited at  $\sim 1200$  and  $\sim 1130\text{ cm}^{-1}$ . The vibration peaks of C—H and  $\text{CH}_3$  of PMMA are also visible at  $1454\text{ cm}^{-1}$  and  $1407\text{ cm}^{-1}$ , respectively. The main characteristic peaks of the NGPE show no clear changes with introducing of different contents of OREC, which means that the addition of OREC does no influence on the polymerization. Briefly, polymerized PMMA in the NGPE system would not interact with other components corresponded to the previous study.<sup>12</sup>

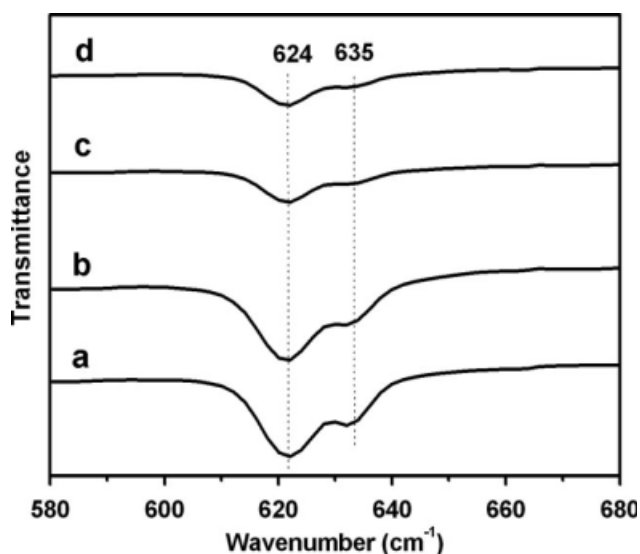
Moreover, the stretching vibration frequency of C=O in PC (an Fermi resonance at  $1790\text{ cm}^{-1}$  and at  $1900\text{ cm}^{-1}$ ) gives rise to less intensive with the introducing of OREC. Hence, it could assume that there is an interaction between C=O of PC and hydroxyl groups of OREC. In the NGPE system, OREC could absorb a certain amount of PC and form the finer exfoliated platelets which well dispersed in the gel system. It can be reasonable to



**Figure 3** FTIR spectras in the wavenumber range of 500–2000  $\text{cm}^{-1}$  of GPE with 0 wt % OREC (a), NGPE with 1 wt % OREC (b), NGPE with 3 wt % OREC (c), and NGPE with 5 wt % OREC (d).

make a hypothesis that a existence of interaction between the OREC and PC, which could effect the interaction between  $\text{Li}^+$  and C=O, thus causing a release of more free  $\text{Li}^+$  to increase ion conductivity.<sup>13,14</sup>

Furthermore, Figure 4 indicates that there is also an interaction between OREC and  $\text{LiClO}_4$ . The  $\nu(\text{ClO}_4^-)$  of the  $\text{LiClO}_4$  shows one peak at  $\sim 624\text{ cm}^{-1}$ , and this peak is assigned to the free anion that does not interact with the lithium cation. Moreover, there is a peak around  $635\text{ cm}^{-1}$ , which could due to the interaction between  $\text{Li}^+$  and  $\text{ClO}_4^-$ .



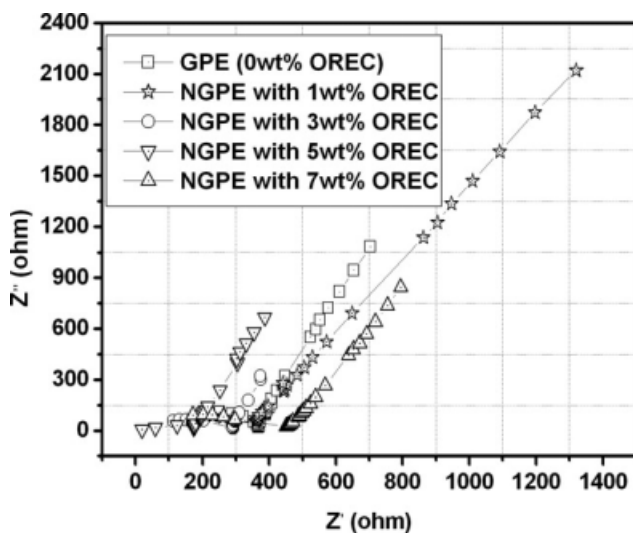
**Figure 4** FTIR spectras in the wavenumber range of 580–680  $\text{cm}^{-1}$  of GPE with 0 wt % OREC (a), NGPE with 1 wt % OREC (b), NGPE with 3 wt % OREC (c), and NGPE with 5 wt % OREC (d).

Moreover, the peak around  $635\text{ cm}^{-1}$  becomes weak with the increasing of OREC content, which means the number of lithium-ion pairs decreases. Those facts are sufficient to indicate that presence of OREC would provide extra dissociation of lithium salts. Moreover, the interaction between the  $\text{Li}^+$  and  $\text{ClO}_4^-$  decreases with the increase of the OREC content; thus it is favorable for acquiring more free  $\text{Li}^+$  to enhance the ion conductivity.<sup>15,16</sup>

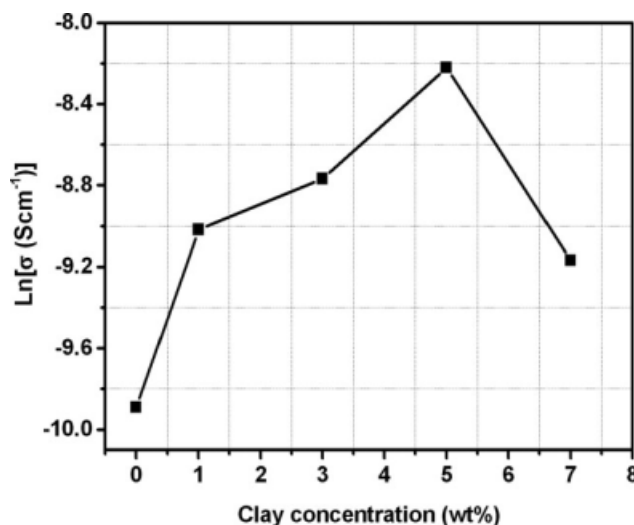
### Electrical properties of the OREC/PMMA

For the polymer electrolyte membrane, electrochemical impedance spectroscopy (EIS) analysis is further performed to understand the influence of OREC on the ionic conductivity of NGPE. Figure 5 shows the impedance plots of nanocomposite gel electrolyte materials.

As shown in Figure 5, the bulk impedance of the NGPE increases first and then decreases with the increasing amount of OREC, the lowest value of the bulk impedance corresponding to the 5 wt % OREC content. Figure 6 shows the effect of OREC content on the ionic conductivity of NGPE at  $25^\circ\text{C}$ . It is obvious to observe that ionic conductivity increases with increasing the OREC content and reaches a maximum value when the OREC content is 5 wt %, and then begin to decrease. As it is described in the FTIR analysis, the electronegative silicate in the nanocomposite with high-dielectric constant could help to dissolve more electrolyte salt ( $\text{LiClO}_4$ ), which means that more free  $\text{Li}^+$  are released in the gel system leading to the increase of the ionic conductivity.<sup>8,17</sup> Moreover, as the amount of OREC over



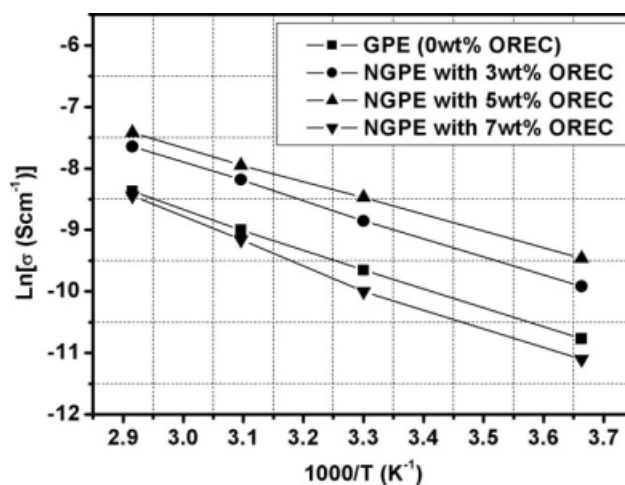
**Figure 5** Alternating current impedance analysis of OREC/PMMA gel electrolyte with OREC content of 0, 1, 3, 5, and 7 wt %.



**Figure 6** Conductivity at  $25^\circ\text{C}$  of NGPE as a function of OREC content.

5 wt %, a decrease in conductivity was detected because  $\text{Li}^+$  transferring will be obstructed by the cluster of gathered OREC.

The ionic conductivity of OREC/PMMA gel electrolytes with different OREC contents at different temperatures is shown in Figure 7. The ionic conductivity of all the samples increases with the increasing of temperature. With the increasing of temperature, the segment motion of polymer chains relaxes more frequently, which offers more free volume for the ion transferring. In the whole temperature range, the NGPE with 5 wt % OREC content exhibits always the highest conductivity values among all the other samples due to its proper content and well disperse status of OREC in the gel system.



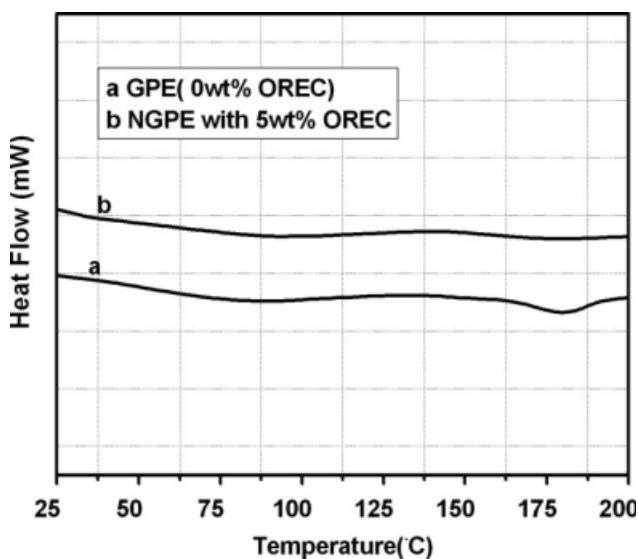
**Figure 7** Ionic conductivity vs. temperature for NGPE membranes with 0, 3, 5, and 7 wt % OREC concentration.

**Thermal stability of OREC/PMMA gel electrolyte**

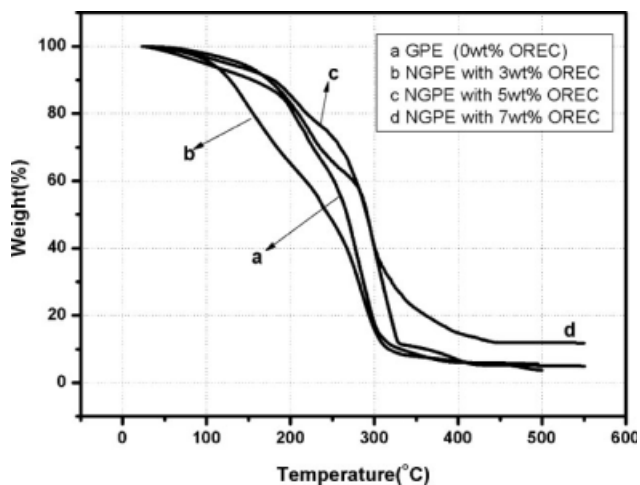
Figure 8 shows the DSC curves of NGPE with 5 wt % OREC addition and unfilled GPE, in the temperature range of 20–200°C. The DSC curve of the NGPE doped with 5 wt % OREC content exhibits a stable trend through the whole temperature range compared with unfilled GPE. There are no exothermic or endothermic peaks in the DSC curve of NGPE/OREC, indicating that no phase transitions are occurred and the NPGE remains in the gel state in the wide temperature range.

To investigate the difference of PC conservation rate between unfilled GPE and NGPE, TGA curves of the NGPE with different OREC contents and unfilled GPE are shown in Figure 9. From room temperature upto 120°C, all the composite NGPE shown less PC weight loss compare to reference GPE.

An intensive attention will be focus on the NGPE with 5 wt % OREC as follows due to its best compromise in terms of exfoliation statuses and improvement of conductivity. In the whole temperature range, the weight loss of GPE is always higher than that of 5 wt % NGPE. In specific, at the same weight loss of 5 wt % corresponding temperature to unfilled GPE and 5 wt % NGPE is 97°C and 124°C, respectively. When considering the matter of final residual weight, composite and unfilled GPE both exhibit similar values. That is obvious to proposed that with an proper content introduction of OREC, silicate layers are exfoliated and dispersed in the gel system, which could suppress PC loss from gel system under lower and medium temperature range. While temperature increases, clay layers would act as catalysis gathering heat facilitated the degradation of the polymer matrix which decreases the thermal



**Figure 8** DSC scans of GPE (a) and NGPE membrane with 5 wt % OREC (b).



**Figure 9** TGA curves of GPE (a) and NGPE membrane with 3 wt % OREC (b), NGPE with 5 wt % OREC (c), and NGPE with 7 wt % OREC (d).

stability at high temperature. In fact, based on same *in situ* procedure of membrane preparation, it could point out that an sufficient enhancement of PC conservation rate is observed by introducing 5 wt % OREC around the working temperature of Lithium-ion battery.

**CONCLUSIONS**

Nanocomposite gel polymer electrolytes doped with high-performing layered organic rectorite were successfully synthesized through *in situ* polymerization with the aim of enhancing its thermal stability and ionic conductivity. In particular, the NGPE sample doped with 5 wt % OREC content improved the performance of unfilled GPE in terms of thermal stability and ionic conductivity in a wide range of temperatures, as evidenced by DSC, TGA, and EIS. This enhancement of performance could be ascribed to the interactions between the constituents in NGPE, as observed by FTIR analysis. The experimental results allow to conclude that the NGPE doped with 5 wt % of OREC is a promising material to be further investigated for the lithium-ion battery.

**References**

1. Chen, H. W.; Lin, T. P.; Chang, F. C. *Polymer* 2002, 43, 5281.
2. Piana, M.; Arrabito, M.; Bodoardo, S.; D'epifanio, A.; Satolli, D.; Croce, F.; Scrosati, B. *Ionics* 2002, 8, 17.
3. Xi, J. Y.; Ma, X. M.; Cui, M. Z.; Huang, X. B.; Zheng, Z.; Tang, X. Z. *Chin Sci Bull* 2004, 49, 785.
4. Deepa, M.; Sharma, N.; Agnihotry, S. A.; Singh, S.; Lal, T.; Chandra, R. *Solid State Ionics* 2002, 152, 253.
5. Agnihotry, S. A.; Ahmad, S.; Gupta, D.; Ahmad, S. *Electrochim Acta* 2004, 49, 2343.
6. Wasiucionek, M.; Breiter, M. W. *J Appl Electrochem* 1997, 27, 1106.

7. Adebahr, J.; Byrne, N.; Forsyth, M. *Electrochim Acta* 2003, 48, 2099.
8. Chen, H. W.; Chang, F. C. *Polymer* 2001, 42, 9763.
9. Ma, X. Y.; Lu, H. J.; Liang, G. Z. *J Appl Polym Sci* 2005, 4, 1165.
10. Ma, X. Y.; Liang, G. Z.; Lu, H. J. *J Appl Polym Sci* 2005, 97, 1915.
11. Huang, Y.; Ma, X. Y.; Liang, G. Z. *J Chin Ceram Soc* 2006, 34, 81.
12. Ostrovskii, D.; Brodin, A.; Torell, L. M.; Appetecchi, G. B.; Scrosati, B. *J Chem Phys* 1998, 109, 7618.
13. Huang, Y.; Ma, X. Y.; Liang, G. Z. *J Chin Ceram Soc* 2006, 34, 465.
14. Huang, Y.; Ma, X. Y.; Liu, H. L. *J Chin Ceram Soc* 2005, 33, 197.
15. Croce, F.; Persi, L.; Scrosati, B.; Serraino-Fiory, F.; Plichta, E.; Hendrickson, M. A. *Electrochim Acta* 2001, 46, 2457.
16. Eneghettia, P.; Qutubuddina, S.; Webber, A. *Electrochim Acta* 2004, 49, 4923.
17. Wang, M. K.; Dong, S. J. *J Power Sources* 2007, 170, 425.