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# Influence of Organophilic Clay on the Morphology, Plasticizer-Maintaining Ability, Dimensional Stability, and Electrochemical Properties of Gel Polyacrylonitrile (PAN) Nanocomposite Electrolytes

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ABSTRACT: Montmorillonite clay was modified with four kinds of quaternary alkylammonium salts to enable the intercalation of polyacrylonitrile (PAN) into the resulting organophilic clay in PC/EC cosolvents. X-ray diffraction experiments revealed that PAN was able to intercalate in the clay galleries. The exfoliation and intercalation phenomena were also confirmed by transmission electron microscopy. A series of gel PAN/clay nanocomposite electrolyte materials were successfully prepared by incorporating appropriate fractions of PAN, organophilic clay, PC/EC cosolvent, and $LiClO_4$. The PAN/clay nanocomposite electrolyte shows a maximum ionic conductivity of $1.4 \times 10^{-2}$ S/cm and exhibits superior ability in film formation and plasticizer absorption, and dimensional stability in comparison to the electrolyte that contains no organophilic clay. Cyclic voltammetric data indicated that the addition of organophilic clay significantly enhances the electrochemical stability of the composite electrolyte system.

## Introduction

To improve our living standard and quality, it is desired that various electronic appliances and related products are compact and user-friendly. Hence, it is a researcher's or designer's dream to improve the functions of each unique product. Among the various functions of the on-market products, wireless, mobile, versatile, lightweight, thin, and compact are most favored. Supplied as a power source, batteries need to meet certain requirements such as safety, weight limit, dimensional restrictions, and definitely environmental awareness. Therefore, the high electric capacity of a lithium polymer secondary battery was produced to meet these requirements. The polymer electrolyte materials in a lithium polymer secondary battery system function as the electrolyte and the separator between anode and cathode. As a result, the ionic conductivity, dimensional stability, and electrochemical stability need to meet a certain standard.[1,2]

Most of the promising candidates for a lithium polymer secondary battery rely on the use of poly(ethylene oxide) (PEO) as a matrix polymer for lithium salts. In these systems, the ether oxygen acts as coordinating site and promotes the dissociation of the salt. A drawback in these systems is the precipitous decrease in conductivity at temperatures below the melting temperature, which is typically above room temperature.[3,4] Recently, one of the most promising ways to improve the electrochemical performance of polymer electrolytes is to form composite electrolytes by adding inorganic fillers and a series of organophilic montmorillonite clays, while retaining their ion-conductivity in the range between $10^{-4}$ and $10^{-6}$ S/cm.[5−8] Poly[bis(methoxyethoxy)ethoxy]phosphazene, MEEP, is one such material that combines the high ion-solvating property of its ethylene oxide side groups and the elastomeric character imparted by the flexible polyphosphazene backbone. Despite its high ionic conductivity, its poor mechanical stability is a disadvantage for feasible use.[9] Hence, to improve its mechanical properties, chemical and radiation cross-linking methods have been applied.[10−13] Regardless of MEEP's promising features, the fundamental conduction properties of the gel electrolytes are not well understood. The gel can be identified as a composite or hybrid material composed of the electrolyte solution and the host polymer. Gelation of the nonaqueous electrolytes solution would mitigate the potential instability against some thermal and mechanical shocks, especially in the package case. Polymers such as polyvinylidene fluoride, poly(methyl methacrylate), or a polyacrylonitrile-based gel film, which has polar groups at the chains, have been applied for the polymer electrolyte of the lithium rechargeable battery, which has a 3 V output voltage and 90−100% Coulombic efficiency.[14−18]

Recently, montmorillonite, a layered material with lamellar shape, has attracted intensive research interest for the preparation of polymer/clay nanocomposites because its lamellar elements display high in-plane strength, stiffness, and high aspect ratio. Typically, the chemical structures of montmorillonite (MMT) consist of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either magnesium or aluminum hydroxide. The $Na^+$ and $Ca^{2+}$ residing in the interlayer regions can be replaced by organic cations such as alkylammonium ions via a cationic-exchange reaction to render the hydrophilic-layered silicate organophilic. According to many recently published related works, the dispersion of nanolayers of mineral clay was found to boost the ionic conductivity,[19] thermal stability,[20] mechanical strength,[21] molecular barrier,[22] and flame-retardant properties of polymers.[23]

In this report, the preparation of a series of gel polyacrylonitrile (PAN)/organophilic clay nanocomposite

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electrolytes with a quaternary alkylammonium salt as the intercalating agent is presented. The influences of adding the organophilic clay into gel polyacrylonitrile electrolytes on their properties such as morphology, ionic conductivity, electrochemical property, plasticizer-maintaining ability, and dimensional stability are also investigated.

## Experiment

**1. Materials.** Polyacrylonitrile ($M_w$: 150 000) was purchased from Polysciences Co., and lithium perchlorate ($LiClO_4$) was ordered from Lancaster Synthesis. Ethylene carbonate (EC), propylene carbonate (PC), and methanol were all obtained from Acros Organics. Dodecyltrimethylammonium bromide, $C_{12}H_{25}N(CH_3)_3Br$, myristyltrimethylammonium bromide, $C_{14}H_{29}N(CH_3)_3Br$, cetyltrimethylammonium bromide, $C_{16}H_{33}N(CH_3)_3Br$, and didodecyldimethylammonium bromide, $[CH_3(CH_2)_{11}]_2(CH_3)_2NBr$, were purchased from Aldrich Chemicals. $LiClO_4$ was dried by vacuum ($<10^{-3}$ Torr) for 24 h at 120 °C prior to usage. All the other reagents and solvents were consumed as received. The montmorillonite clays (PK802, PK805) were supplied by Paikong Ceramic Materials Co.

**2. Preparation of Organophilic Clay.** The organophilic clay was prepared by cation-exchange reaction between the sodium cations of MMT clays (PK802, PK805) and four kinds of quaternary alkylammonium cations ($C_{12}H_{25}(CH_3)_3N^+$, $C_{14}H_{29}(CH_3)_3N^+$, $C_{16}H_{33}(CH_3)_3N^+$, $[CH_3(CH_2)_{11}]_2(CH_3)_2N^+$) of intercalating agents. The equation for calculating the intercalating agent used for a cation-exchange reaction is listed below:

$$98/100 \times 5\text{ g (for clay)} \times 1.2 = (X/M_w \text{ of intercalating agent}) \times 1 \times 1000$$

where $X$ represents the amount of used intercalating agent, 98/100 represents the CEC value per 100 g of MMT clay (PK805), (PK802: 95/100), and 1.2 (>1) indicates the excess amount of intercalating agent used. The modified procedure described below was followed for the preparation of organophilic clays (*o*-pk802, *o*-pk805).

**3. Preparation of Polyacrylonitrile/Clay Nanocomposites.** Different amounts of organophilic clay (1, 3, 5, 7, or 9 wt %) were mixed individually with 10 mL of PC/EC cosolvent (1/1 in volume ratio). A typical procedure for the preparation of PAN/clay nanocomposite material with 3 wt % clay loading is described below. First, an appropriate amount of organophilic clay (0.03 g) was introduced into 10 mL of PC/EC cosolvent under stirring for 12 h at room temperature. Then, 0.97 g of PAN powder was added to the PC/EC cosolvent in another bottle, and the resulting mixture was stirred for 12 h at 80 °C until the polymer solution was homogeneous. Second, the organophilic clay solution was added to the polymer solution under stirring for 12 h at 60 °C. The PAN/clay films were prepared by casting the solution onto glass plates. The films were allowed to dry in a vacuum oven ($10^{-2}$ Torr) for 24 h at 60 °C. The thickness of the films was 0.2 mm approximately.

**4. Preparation of Gel PAN/Clay Nanocomposite Electrolytes.** In the preparation process, first, an appropriate amount of organophilic clay (0.03 g) was introduced into a solvent such as EC/PC (1/1 in volume ratio) under stirring for 12 h at room temperature. Second, this clay solution was added into the polymer solution (0.97 g/10 mL) that was obtained from the above process (refer to "Experiment", paragraph no. 3), and the resulting mixture was continuously stirred for 12 h at 80 °C. The concentration of lithium salt is expressed as the molar ratio of salt fed to a PAN repeat unit, $F = [LiClO_4]/[CH_2CH(CN)]$. The mixed solution of polymer and organophilic clay solution was dropped into 3 mL of EC/PC to dissolve the lithium salt under stirring for 6 h at 60 °C. The gel PAN electrolyte films were prepared by casting the solution onto a glass plate. The partial solvent was removed from the films in the vacuum system at 60 °C. The thickness of the films varied between 50 and 100 $\mu$m. The free-standing films of gel PAN nanocomposite electrolytes with solvent containing 15−90% were successfully prepared. The electrolyte films were stored inside the glovebox.

**Table 1. 2$\theta$ and *d*-Spacing (Å) Values of Treating Organophilic PK805 with the Different Quaternary Ammonium Bromides**

| quaternary ammonium bromide | 2$\theta$ | *d*-spacing (Å) |
|---|---|---|
| $C_{12}H_{25}N(CH_3)_3Br$ | 5.28 | 16.724 |
| $C_{14}H_{29}N(CH_3)_3Br$ | 4.92 | 17.947 |
| $C_{16}H_{33}N(CH_3)_3Br$ | 4.70 | 18.786 |
| $[CH_3(CH_2)_{11}]_2(CH_3)_2NBr$ | 4.02 | 21.962 |

**5. Instrument.** Wide angle X-ray diffraction study of the samples was performed on a Rigaku D/MAX-3C OD-2988N X-ray diffractometer with copper target and nickel filter at the scanning rate 1°/min. The samples for transmission electron microscopy (TEM) study were first prepared by putting films of PAN/clay nanocomposite into epoxy resin capsules followed by curing the epoxy resin at 70 °C for 24 h in a vacuum oven. Then, the cured epoxy resin containing PAN/clay nanocomposite was microtomed with a Reichert-Jumg Ultracut-E into 60−90 nm thick slices. Subsequently, one layer of carbon about 10 nm thick was deposited on these slices on mesh 100 copper nets for TEM observation on a JEOL-200FX with an acceleration voltage of 160 kV. DSC measurements were implemented with a Seiko DSC 200. Typically, the samples were heated first at the rate 10 °C/min to 125 °C and immediately cooled back to the initial temperature. This was followed by another heating cycle to study possible thermal hysteresis.

Ionic conductivity measurements were carried out under vacuum using a HP4192A impedance analyzer at room temperature over the frequency range 5−13 MHz. The films of gel polymer electrolyte were sandwiched between two gold electrodes. The plating−stripping process of lithium was evaluated from the CV curves obtained in the three-electrode cell having a stainless steel working substrate, a lithium counter electrode, and a lithium reference electrode. The CV curves were collected with a Eco Chemie BV model PGSTAT30 potentiostat/galvanostat coupled with a personal computer. The thermal mechanical analyses (TMA) for the free-standing films of gel PAN electrolyte were carrying out from −60 to 120 °C with a Perkin-Elmer DMA 7e analyzer at the heating rate 5 °C/min.

## Results and Discussion

**1. Modification of Organophilic Clay.** Montmorillonite (MMT) was made organophilic by reacting it with quaternary ammonium salts. Montmorillonite is a clay containing stacked silicate sheets measuring ~10 Å in thickness and ~2180 Å in length, and the silicate sheets can exchange their cations with the hydrophilic end of quaternary ammonium salts.[24] Through this ion-exchange reaction, the long alkyl group of quaternary ammonium intercalated in the MMT clay galleries and enlarged the distance between the layers. The enlarged distance would facilitate the intercalation of polymer chain into the organophilic clay. The X-ray diffraction analysis indicated that, under the same operational conditions, the distance between the clay interlayers varied with the type of quaternary ammonium salts. Table 1 illustrates that the distance stretched by didodecyldimethylammonium bromide, $[CH_3(CH_2)_{11}]_2(CH_3)_2NBr$, was the largest. The may be due to the structure and bonding angle of the two long-chained alkyl groups, which showed a bumper jack morphology between the two dodecyl groups and the clay interlayers. This "bumper jack" effectively enlarged the distance between the interlayers to 22 Å (the original distance was 12 Å).

**2. Polyacrylonitrile Dispersed the Organophilic Clay.** Polyacrylonitrile solution was mixed with 3%

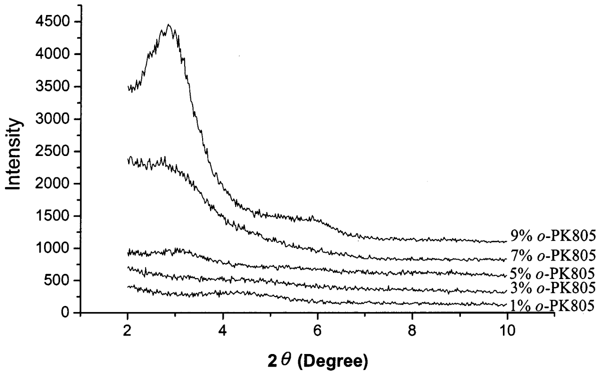

**Figure 1.** Various X-ray diffraction patterns by adding different amounts of *o*-PK805 into polyacrylonitrile.

organophilic clay into a transparent solution. A 0.2 mm thick film was then obtained by casting this solution on a glass plate. The X-ray diffraction pattern of this film indicated that the characteristic $2\theta$ (4.02°) observed for pure organophilic clay disappeared in this PAN/clay film, suggesting that the polymer chain of PAN has completely exfoliated in the clay nanolayers. To further study this, different amounts of organophilic clay (1%, 3%, 5%, 7%, and 9%) were mixed respectively with PAN solution to prepare films of the same thickness, and X-ray diffraction patterns were recorded for these films and displayed in Figure 1. This figure shows that the XRD pattern changed significantly with the increase of organophilic clay in the PAN/clay film. The XRD patterns of the films containing 1% and 3% organophilic clay are very similar in that no diffraction peaks at $2\theta$ were observed in these patterns, indicating that exfoliation exists in these two composite materials. When the amount of organophilic clay in the composite increased to 5%, a small peak near $2\theta = 3°$ gradually appeared. This particular peak became more significant as the amount of organophilic clay was increased to 7% and 9%, indicating that the molecular chain of PAN solution still intercalated between the clay layers. The fact that the $2\theta$ angle changed from 4.02° to 3°, when the amount of organophilic clay in the PAN/clay is increased from 0 to higher than 3%, indicates that the PAN/clay nanocomposite is intercalating. The diffusion of clay in the polymer chain was examined with a PAN/clay mixture containing 5% clay using transmission electron microscopy. The micrograph is shown in Figure 2. When the specific regions were observed, both the destroyed exfoliation of the clay nanolayers and the intercalation are less obvious. The PAN/5% organophilic clay nanocomposites demonstrate both the exfoliation and intercalation. This conclusion is consistent with the X-ray result. By TEM we observe that the nanolayers of organophilic clay well diffused in the polymer chain, indicating that it may change the morphology of polyacrylonitrile. Differential scanning calorimetery (DSC) was used to observe the different crystallizations of polyacrylonitrile without clay and with added clay. Figure 3 shows that, the melting endotherm peak area is gradually reduced with addition of organophilic clay at around 80 °C. It is suggested that the polyacrylonitrile with organophilic clay destroys the order within the crystalline domains and that the morphology of polyacrylonitrile tends to be amorphous. It is apparent that the conductivity of the polymer electrolyte is enhanced.[25]

**Figure 2.** TEM micrograph of the PAN filled with 5 wt % *o*-PK805.

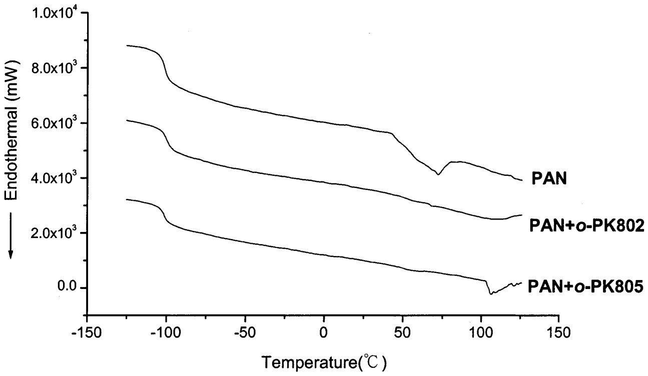

**Figure 3.** DSC heating curves of PAN and PAN/clay (3%) nanocomposite materials.

**3. Plasticizer-Maintaining Ability.** The major difference between gel polymer electrolytes and solid polymer electrolytes lies in the presence of the polymer system plasticizer. Relevant literature pointed out that the presence of plasticizer enhances the ionic conductivity but results in poor dimensional stability, poor mechanic strength, and poor film formation. In this study, a series of gel polymer electrolytes with film thickness between 50 and 100 $\mu$m were prepared with the addition of 3% organophilic clay and $LiClO_4$ (with different $F$ values) into PAN. It is found that the clay-containing polymer electrolyte is superior to the clay-free polymer electrolyte. To understand whether the organophilic clay helps in maintaining the plasticizer in the gel polymer electrolyte film, both clay-containing and clay-free polymer electrolytes were kept in a 0.1 Torr vacuum oven at 50 °C, and the amount of plasticizer reduced with time was recorded and the data are

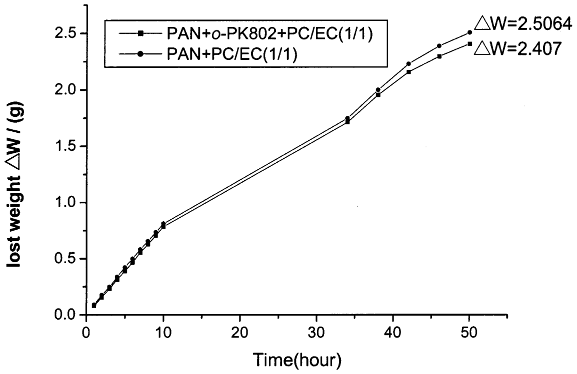

**Figure 4.** Comparison of plasticizer-maintaining ability in different gel PAN/organophilic clay electrolyte materials.

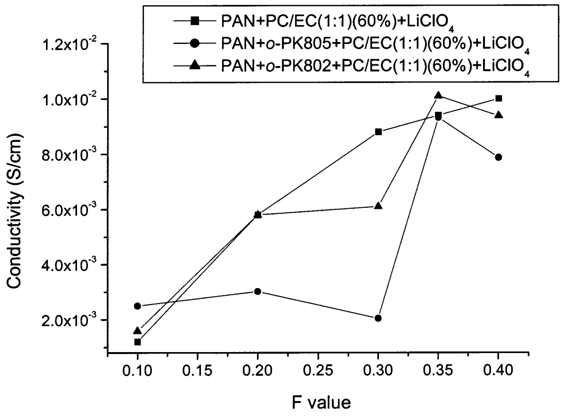

**Figure 5.** Conductivities versus $LiClO_4$ content (*F* value) for gel PAN nanocomposite electrolytes containing various organophilic clays at room temperature.

collected in Figure 4. The data in this figure suggest that as the time increased the organophilic clay indeed improved the plasticizer-maintaining ability.

**4. Conductivity.** The effect of the addition of organophilic clay on the conductivity of the resulting polymer electrolyte is demonstrated in Figure 5. This figure shows that the conductivity of gel polyacrylonitrile electrolyte with addition of organophilic clay was not superior to that of the one free of organophilic clay. The reason may be described herein. Though the condition of broken nanolayers of organophilic clay proportionally dispersed in the polymer electrolyte is helpful to let the polyacrylonitrile morphology be amorphous, it also is an impediment to extending the movement path of the lithium ion, as Figure 6 shows. This causes the variance of conductivity to be larger as we add organophilic clay to the gel polyacrylonitrile electrolyte. And the conductivity does not improve as the amount of lithium perchlorate increases. Normally, the conductivity will be enhanced with increasing amount (*F* value) of lithium salt; for example, the conductivity of the gel polyacrylonitrile electrolyte without adding the organophilic clay will be enhanced as the *F* value is increased. The data collected in Table 2 and illustrated in Figure 5 reveal that the conductivity is related to the lithium salt concentration.

**Figure 6.** Micrograph showing impediment of the extent of the lithium ion movement path.

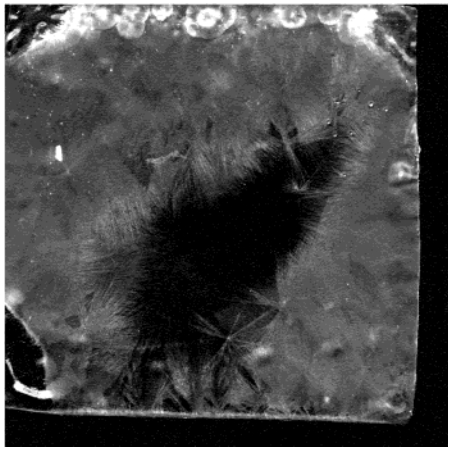

**Figure 7.** Desk-top scanner obtained crystalline image of the gel PAN electrolyte film.

During the process of preparing the polymer electrolyte film, accidentally, we found the distinct appearance visible to the naked eyes of the lithium perchlorate crystal forming gradually in the film as we were reducing the solvent amount (30% lower) in the film free of organophilic clay, as Figure 7 shows. But such an appearance could not easily be found in the film with added organophilic clay. It comes down to this: it is indeed conducive to let the polymer chain be amorphous while the nanolayers of organophilic clay disperse in polymer electrolyte and also to make the $Li^+$ and $ClO_4^-$ recrystallize uneasily, to form many free $Li^+$ to be electrical charge carrier, which is helpful for conductivity. On the basis of this reason, the conductivity of the gel polyacrylonitrile electrolyte with added organophilic clay was $1.0 \times 10^{-2}$ S/cm higher yet extend the movement path of $Li^+$.

The effect of plasticizer quantity was studied. And it was found that although the appearances of the polymer electrolyte films were not altered significantly by the plasticizer quantity, the increase of plasticizer degraded

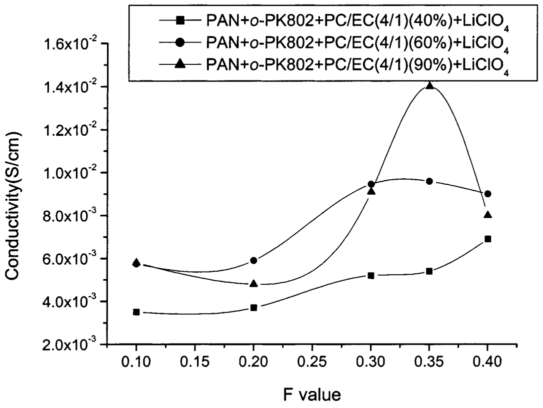

**Figure 8.** Plasticizer ratio variation of conductivity with $LiClO_4$ concentration in gel PAN nanocomposite electrolytes containing organophilic clay (3%) at room temperature.

the mechanic strength and the film formation. As illustrated in Figure 8, the conductivity was improved significantly with the increase of plasticizer, especially in the case of PC/EC cosolvent and $F$ value = 0.35. For example, conductivity was increased up to 3−4 times when the percentage of PC/EC cosolvent was increased from 40% to 90%. However, if the percentage of solvent exceeded 70%, the polymer electrolyte film become less smooth and was subjected to solvent-leaking problems. Consequently, the variation in the conductivity might be greater, as can be referenced to the data in Table 3.

**5. Dimensional Stability.** In a lithium polymer secondary battery, the polymer electrolyte is employed as both electrolyte and separator. The heat generated during the charging/discharging process of a battery may cause the deformation of the polymer electrolyte, leading to a lower charging/discharging efficiency and even a short circuit. Therefore, superb dimensional stability is essential for a polymer electrolyte to be used in battery applications.

Thermal mechanical analysis (TMA) was performed for PAN polymer electrolyte containing 3% organophilic clay, 15% PC/EC cosolvent, and $LiClO_4$ ($F = 0.25$). The thermal expansion coefficients of this organophilic clay containing PAN polymer electrolyte were recorded within a certain temperature range and compared to the coefficients recorded for the PAN polymer electrolyte without the addition of organophilic clay. As shown in Figure 9, within the temperature range 30−75 °C, the thermal expansion coefficient of the organophilic clay containing PAN electrolyte is $778 \times 10^{-6}$ mm/°C whereas the thermal expansion coefficient of the clay-free PAN electrolyte in the same temperature range is $3400 \times 10^{-6}$ mm/°C. In addition, the maximum thermal deformation temperature of the organophilic clay containing PAN was enhanced from 75 to 95 °C. This result indicates that the addition of clay enhances the dimensional stability of the polymer electrolyte films. Such enhanced dimensional stability of the gel PAN nanocomposite electrolyte can be related to the facts that the nanolayers of the organophilic clay, that resulted from the exfoliating process, spread out evenly between the polymer chains of PAN and that the intermolecular interactions between the polymer and the nanolayers were fairly stable.

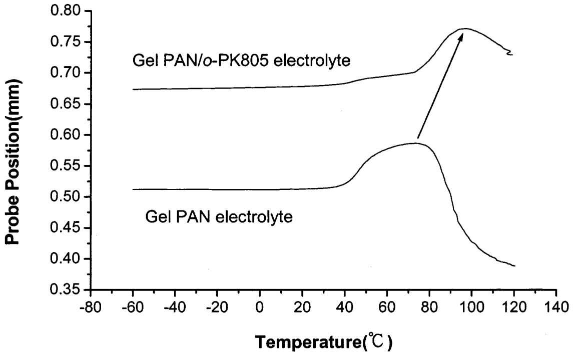

**Figure 9.** Comparison of thermal expansion curves in different gel PAN composite electrolytes.

**6. Electrochemical Stability.** The gel polymer electrolyte films with superior conductivity were selected for the electrochemical studies. In the half-cell, Li/GPEs/Li is used as the counter and reference electrodes and a piece of Pt plate is used as the working electrode. The assembly was put in a storage tank filled with argon gas. Cyclic voltammetry was performed to study the plating−stripping cycling effect of lithium. It is found that the organophilic clay-containing PAN electrolyte film exhibits an anodic decomposition potential at around 4.2 V. Furthermore, as Figure 10 shows, the addition of organophilic clay (*o*-PK805) apparently facilitates the redox cycling of lithium in the gel PAN nanocomposite electrolyte. It is possible that the organophilic clay enables more plasticizer to be included into the polymer electrolyte film, and the highly dielectric plasticizer would dissociate the lithium salt more effectively and disperse the lithium ion evenly in the polymer electrolyte, increasing the reversibility of lithium ion in losing and gaining electrons. Hence, this effect is beneficial for future research on the rechargeable cyclic effect in lithium polymer secondary batteries.

**Table 2. Conductivities (S/cm) of Gel Polyacrylonitrile Electrolytes (GPEs) with Various $LiClO_4$ Contents and Organophilic Clays**

| | conductivity (S/cm) | | | | |
|---|---|---|---|---|---|
| GPE nanocomposite | $F = 0.1$ | $F = 0.2$ | $F = 0.3$ | $F = 0.35$ | $F = 0.4$ |
| PAN + $LiClO_4$ + PC/EC (1/1) (60%) | $1.2 \times 10^{-3}$ | $5.8 \times 10^{-3}$ | $8.8 \times 10^{-3}$ | $9.4 \times 10^{-3}$ | $1.0 \times 10^{-2}$ |
| PAN + *o*-PK805 + $LiClO_4$ + PC/EC (1/1) (60%) | $2.5 \times 10^{-3}$ | $3.0 \times 10^{-3}$ | $2.0 \times 10^{-3}$ | $9.3 \times 10^{-3}$ | $7.9 \times 10^{-3}$ |
| PAN + *o*-PK802 + $LiClO_4$ + PC/EC (1/1) (60%) | $1.6 \times 10^{-3}$ | $5.8 \times 10^{-3}$ | $6.1 \times 10^{-3}$ | $1.0 \times 10^{-2}$ | $9.4 \times 10^{-3}$ |

**Table 3. Conductivities (S/cm) of Gel Polymer Nanocomposite Electrolytes with Various Solvent Contents and $LiClO_4$ Contents**

| | conductivity (S/cm) | | | | |
|---|---|---|---|---|---|
| GPE nanocomposite | $F = 0.1$ | $F = 0.2$ | $F = 0.3$ | $F = 0.35$ | $F = 0.4$ |
| PAN + *o*-PK802 + $LiClO_4$ + PC/EC (4/1) (40%) | $3.5 \times 10^{-3}$ | $3.7 \times 10^{-3}$ | $5.2 \times 10^{-3}$ | $5.4 \times 10^{-3}$ | $6.9 \times 10^{-3}$ |
| PAN + *o*-PK802 + $LiClO_4$ + PC/EC (4/1) (60%) | $5.7 \times 10^{-3}$ | $5.9 \times 10^{-3}$ | $9.5 \times 10^{-3}$ | $9.6 \times 10^{-3}$ | $9.0 \times 10^{-3}$ |
| PAN + *o*-PK802 + $LiClO_4$ + PC/EC (4/1) (90%) | $5.8 \times 10^{-3}$ | $4.8 \times 10^{-3}$ | $9.1 \times 10^{-3}$ | $1.4 \times 10^{-2}$ | $8.0 \times 10^{-3}$ |

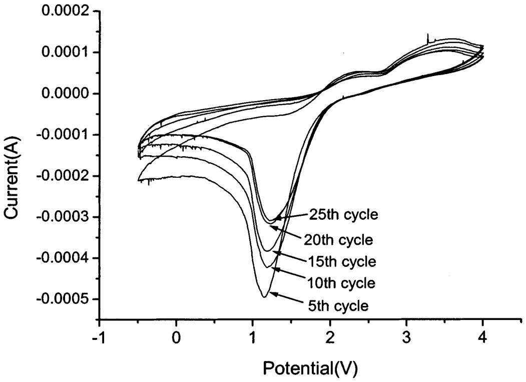

**Figure 10.** Cyclic voltammetric curve of Li/GPEs/Li cell. Lithium metal was used as counter and reference electrode (scan rate 1 mV/s).

## Conclusion

In this work, two types of modified organophilic clays (*o*-PK802 and *o*-PK805) were employed to improve the properties of gel polyacrylonitrile electrolytes. The results indicate that the use of the quaternary alkylammonium salts successfully enlarges the distances between the montmorillonite clay interlayers to 22 Å. This allows the polyacrylonitrile ($M_w$ = 150 000) to enter the interlayers of the organophilic clay (even exfoliation has occurred), forming a series of organic–inorganic hybrid materials. The addition of organophilic clay not only increased the amount of plasticizer but also extended the time period that the plasticizer can stay in the gel PAN nanocomposite electrolyte system. The dispersion of the inorganic nanolayers, resulting from exfoliation, into the polyacrylonitrile electrolyte improves the conductivity and electrochemical stability of the films. For instance, the addition of *o*-PK802 and PC/EC cosolvent (4/1 in volume ratio) could achieve a maximum conductivity of $1.4 \times 10^{-2}$ S/cm. The silicate nanolayers of montmorillonite clay proportionally dispersed in the gel polyacrylonitrile electrolyte are helpful to make the polyacrylonitrile morphology amorphous and, indeed, improve the plasticizer-maintaining ability. However, the conductivity of gel polyacrylonitrile electrolytes with added montmorillonite clay may not be superior to that of the one free of montmorillonite clay.

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