

# Physical and Electrochemical Properties of Low Molecular Weight Poly(ethylene glycol)-Bridged Polysilsesquioxane Organic–Inorganic Composite Electrolytes via Sol–Gel Process

C. Y. Yuan,<sup>1</sup> S. Y. Chen,<sup>1</sup> J. C. Tang,<sup>2</sup> H. C. Yang,<sup>3</sup> Y. W. Chen-Yang<sup>1</sup>

<sup>1</sup>Department of Chemistry, Center for Nanotechnology and R&D Center for Membrane Technology, Chung Yuan Christian University, Chung-Li, Taiwan 32023, Republic of China

<sup>2</sup>Department of Chemical Engineering, Chin Min Institute of Technology, Miaoli, Taiwan 357, Republic of China

<sup>3</sup>Department of Cosmetic Science and Applications, Chin Min Institute of Technology, Miaoli, Taiwan 357, Republic of China

Received 28 April 2006; accepted 20 August 2006

DOI 10.1002/app.25367

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A new class of ionic conducting organic/inorganic hybrid composite electrolyte with high conductivity, better electrochemical stability and mechanical behavior was prepared through the sol–gel processing between ethylene-bridged polysilsesquioxane and poly(ethylene glycol) (PEG). The composite electrolyte with 0.05 LiClO<sub>4</sub> per PEG repeat unit has the best conductivity up to 10<sup>−4</sup> S/cm at room temperature with the transference number up to 0.48 and an electrochemical stability window as high as 5.5 V versus Li/Li<sup>+</sup>. Moreover, the effect of the PEG chain length on the properties of the composite electrolyte has also been studied. The interactions between ions and polymer have also been investigated

for the composite electrolyte in the presence of LiClO<sub>4</sub> by means of FTIR, DSC, and TGA. The results indicated the interaction of Li<sup>+</sup> ions with the ether oxygen of the PEG, and the formation of transient crosslinking with LiClO<sub>4</sub>, resulting in an increase of the *T<sub>g</sub>* of the composite electrolyte. The VTF-type behavior of the ionic conductivity implied that the diffusion of the charge carriers was assisted by the segmental motions of the polymer chains. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2752–2758, 2007

**Key words:** organic–inorganic; polysilsesquioxane; poly(ethylene glycol); ionic conductivity

## INTRODUCTION

Solid polymer electrolytes have attracted widespread interest in recent years. These promising materials are potential for various applications such as rechargeable batteries, data storages, sensors, fuel cells, electrochromic, and photoelectrochemical devices.<sup>1–3</sup> Recently, solid polymer electrolytes applied in the lithium polymer batteries are now being widely studied and developed as rechargeable energy sources, the most important of which is for high energy density batteries.<sup>4</sup>

It is well established that ion conduction takes place predominantly in the amorphous region, and that high segmental mobility of the polymers corresponding to low glass transition temperature (*T<sub>g</sub>*) ensures high mobility of the dissociated ions. The increasing volume fraction of the amorphous domains and the

decreasing *T<sub>g</sub>* appear to be the main path toward obtaining better ionic conductivity.<sup>2,5,6</sup> For these reasons, many researches were conducted regarding the development of new polymer electrolyte.<sup>7</sup>

At the same time, low molecular weight poly(ethylene glycol) (PEG) has the above advantage of having relatively high ambient ionic conductivity (10<sup>−4</sup> S/cm), when complexed with alkali-metal salt. However, their poor mechanical strength cannot satisfy the requirement for solid-state processing.

Recently, hybrid organic–inorganic solid polymer electrolytes, called as ormolytes (an abbreviation of organically modified electrolytes), were demonstrated to enhance the mechanical, thermal, and chemical stability as well as ionic conductivity by introducing inorganic components into these materials.<sup>8–16</sup> The ormolyte properties are strongly dependent on the connectivity of the two phases and the mobility of both the structure network and the active ionic species. This connectivity can be partially controlled by the chemistry, leading to two main families. In Type I nanocomposites, hydrogen bonds and van der Waals interactions associate the organic and inorganic components, while in Type II materials, these two phases are linked together through covalent bonds. Inorganic

Correspondence to: Dr. Y. W. Chen-Yang (erophant@chemer.cycu.edu.tw).

Contract grant sponsors: National Science Council and Chung Yuan Christian University of Taiwan, Republic of China; contract grant number: NSC 92-2745M-033-001.

*Journal of Applied Polymer Science*, Vol. 103, 2752–2758 (2007)  
© 2006 Wiley Periodicals, Inc.

salts can be dissolved in both types of materials, resulting in good solid polymer electrolytes.

In addition, bridged polysilsesquioxanes are a family of hybrid organic/inorganic materials prepared by sol-gel processing of monomers that contain a variable polymer-bridging group and two or more functional silyl groups. The organic group, covalently attached to the trialkoxysilyl groups through Si—C bonds, can be varied in length, rigidity, geometry of substitution, and functionality. This variability provides an opportunity to explore how the organic structural unit contributes to bulk properties such as porosity, thermal stability, optical clarity, chemical resistance, dielectric constant, and compatibility.<sup>8,17–22</sup>

To enhance the interaction between PEG and the silica phase, in this study, a series of organic-inorganic composite electrolytes consisting of low molecular weight PEG ( $M_w$ : 200, 400, and 1000) and bridged polysilsesquioxanes were prepared by sol-gel process, using BTSE as the sol-gel precursor. The as-prepared composite electrolytes not only attained high ionic conductivity by preventing the formation of crystalline structure but also attained high mechanical strength. The A.C. impedance measurement was used to obtain the ionic conductivity properties, the DSC analyses were applied to investigate the phase transitions in these composite polymer electrolytes, and the thermogravimetric analysis were performed to characterize the thermal stability. The ion-polymer and ion-ion interactions were studied on the basis of FTIR spectroscopy. Finally, the cation transport number of the composite electrolytes was measured to determine the effect of the bridged polysilsesquioxanes silica on the conductivity.

## EXPERIMENTAL

### Material

Poly(ethylene glycol)s (PEGs,  $M_w$ : 200, 400, and 1000, Aldrich) were dehydrated at 80°C under vacuum for 24 h before use. Lithium perchlorate ( $\text{LiClO}_4$ , Aldrich) was dried at 120°C under vacuum for 48 h. Bis(triethoxysilyl)ethane (BTSE, Gelest, Tullytown, PA) was used without further purification.

### Preparation of the bridged polysilsesquioxane-containing composite electrolytes

The bridged polysilsesquioxane-containing composite electrolytes were prepared through sol-gel process. The concentration of salt is expressed as the molar ratio of the salt fed to the polyethylene glycol repeat unit,  $F = [\text{LiClO}_4]/[\text{EO}]$ . First, the required quantity of  $\text{LiClO}_4$  was dissolved with an appropriate amount of PEG ( $M_w$ : 200, 400, and 1000) and water. Then, the precursor for sol-gel process, BTSE, was added into

the solution in weak acid conditions, stirring and heating until all the solution became a transparent monophasic liquid. After this, the solution was poured on a flat PE plate. Gelation occurred in a few minutes and the samples were dried slowly in a vacuum oven at a proper temperature for at least 6 days to obtain the composite electrolytes. The dried composite electrolytes were stored in an argon-filled glove box for further measurements.

### Instruments

The ionic conductivities of the electrolytes were determined by the complex impedance method in the temperature range from 30 to 80°C. The sample was sandwiched between stainless steel blocking electrodes and placed in a temperature-controlled oven at vacuum for at least hours before the measurement. The experiments were performed in a constant-volume cylindrical cell with an electrode area of 1.76 cm<sup>2</sup>. The impedance measurements were carried out on a HP 4192A in the frequency range from 1 Hz to 1 MHz. The transference numbers were measured using the technique reported.<sup>23</sup> The electrochemical cell comprised a rectangular piece of composite electrolytes sandwiched between two nonblocking electrodes made of lithium foil, measured with an Autolab PGSTAT 30 potentiostat/galvanostat analyzer.

Infrared absorption spectra were recorded on a BIO-RAD-FTS-7 with a wavenumber resolution of 4 cm<sup>-1</sup>. The sample was mixed with KBr and compressed to form a thin film for the measurement. A SEIKO TG/DTA-220 thermal analyzer (TGA) was used to measure the thermal stability at a heating rate of 10°C/min from 30 to 600°C in nitrogen. The DSC analyses were carried out using a SEIKO SSC-5200 calorimeter with a heating rate of 10°C/min from -150 to 100°C under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

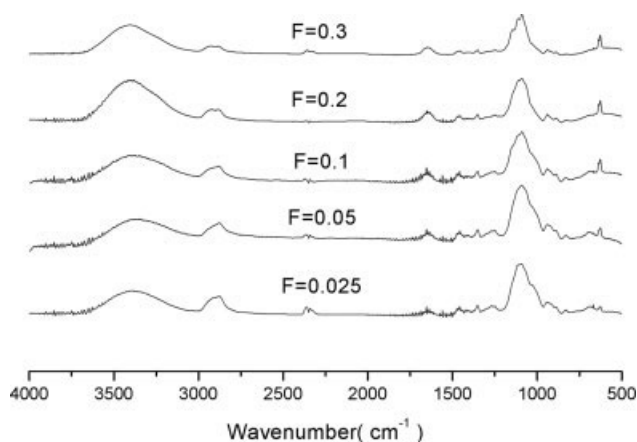
A series of the composite polymer electrolytes were prepared on the basis of low molecular poly(ethylene glycol) (PEG) gelled with bis(triethoxysilyl)ethane (BTSE) in different compositions in the presence of lithium perchlorate ( $\text{LiClO}_4$ ) acting as ionic source. The ethoxysilane groups ( $\equiv\text{Si}-\text{OCH}_2\text{CH}_3$ ) on BTSE can be hydrolyzed into silanol groups ( $\equiv\text{Si}-\text{OH}$ ) by the 6-equivalent  $\text{H}_2\text{O}$  in the presence of acid-catalyst and subsequently can undergo self-condensation reactions to produce siloxane bonds ( $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ ). In addition, hydroxyl groups of PEG are covalently attached to silanol groups of organosilica. A similar behavior has been reported for TEOS-PEG- $\text{LiClO}_4$  electrolytes.<sup>11</sup> The apparent mechanical property of the obtained hybrids depends upon the weight ratio of PEG/BTSE used.

Crack hybrids are obtained for smaller ratios of PEG in the material. However, PEG appeared slightly on the surface of hybrids are obtained for higher ratios of PEG. The resulted composite electrolytes with the weight ratio of PEG/BTSE to be 1.5 are transparent and in good shape over the investigated amounts of LiClO<sub>4</sub>. In this article, the bridged polysilsesquioxane-containing composite electrolytes, BTSE-PEG-LiClO<sub>4</sub>, with  $F = 0.025$ –0.3 of LiClO<sub>4</sub> and 1.5 ratio of PEG/BTSE have been prepared. The properties of the composite electrolytes are analyzed and discussed as follows.

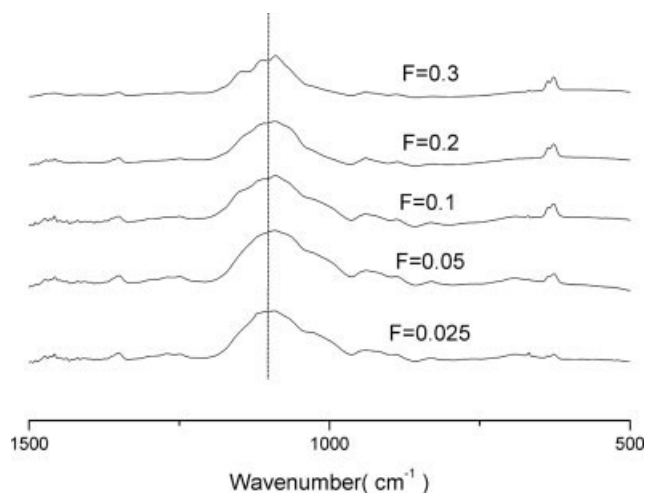
### FTIR spectroscopy

To investigate the network structure and the effect of salt concentration on the phase morphology in the BTSE-PEG-LiClO<sub>4</sub> composite electrolytes, the FTIR spectra have been measured and analyzed.

Figure 1 shows the FTIR spectra of the BTSE-PEG200-LiClO<sub>4</sub> composite electrolytes with the LiClO<sub>4</sub> concentration ranging from  $F = 0.025$ –0.3. It is clearly seen that the characteristic absorption bands for the –OH and –C–O–C– stretching vibrations are observed at 3700–3150 cm<sup>-1</sup> and 1200–1050 cm<sup>-1</sup>, respectively. The absorption band at ~1034 cm<sup>-1</sup> is assigned to the asymmetric stretching of Si–O–Si. The band observed at around 942 cm<sup>-1</sup> is the characteristic vibration of the symmetric ClO<sub>4</sub><sup>-</sup> stretching of the solvent-separated ion pairs [Li(PEG)<sub>*n*</sub>ClO<sub>4</sub><sup>-</sup>].<sup>24,25</sup> The weak band at ~880 cm<sup>-1</sup>, which is the characteristic of the metal-oxygen breathing motion, and provides evidence for the formation of EO salt and crown ether complexes.<sup>26,27</sup> The band at 625 cm<sup>-1</sup> is assigned to the stretching modes of free ClO<sub>4</sub><sup>-</sup> ion.<sup>28</sup> As evidenced from Figure 1, it is obvious that as the concentration of LiClO<sub>4</sub> salt in the composite polymer complexes increases, the frequencies and intensities of the characteristic bands change significantly, indicating that introduction of the salt in the composite electrolytes can



**Figure 1** FTIR spectra of BTSE/PEG200 polymer electrolytes.

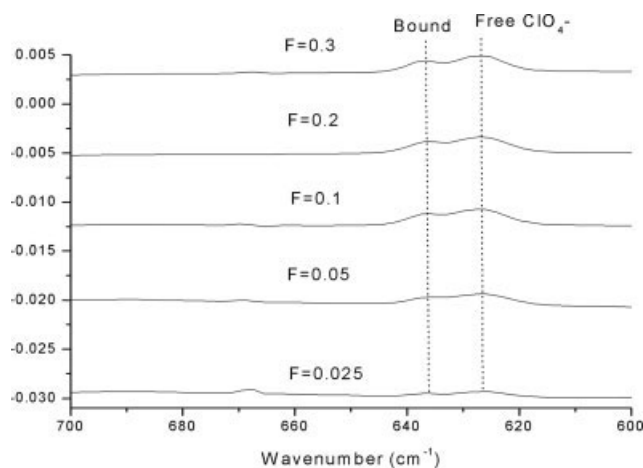


**Figure 2** FTIR spectra of the C–O–C stretching for BTSE/PEG200 polymer electrolytes.

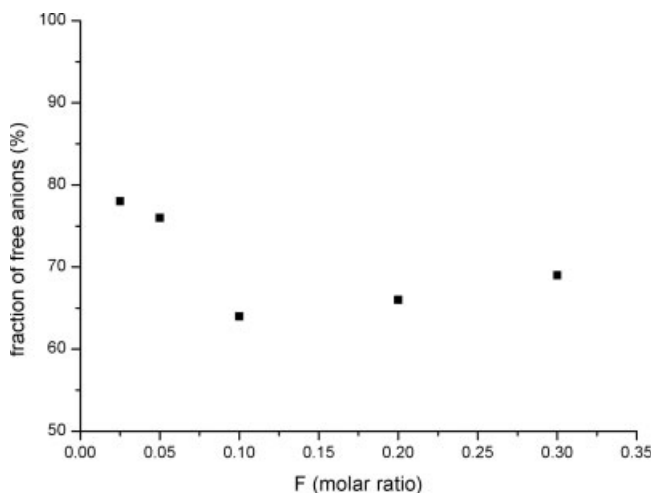
change the intermolecular interactions. In addition, a further hydroxyl stretching vibration is detected around 3250 cm<sup>-1</sup> for each composite electrolytes, which can be ascribed to the O–H stretching vibration of the hydroxyls hydrogen-bonded to –OH groups.<sup>29</sup>

Moreover, the decrease in the position of the C–O–C stretching maximum in the 1100–1110 cm<sup>-1</sup> can be noticed with an increase in the salt concentration in Figure 2. The downshift of the maximum of the C–O–C stretch evidenced the formation of the polymer-salt complex, which is connected with the formation of the transient crosslinks in the electrolyte.<sup>3,30</sup>

In Figure 3, the spectra obtained for the BTSE-PEG-LiClO<sub>4</sub> composite electrolytes in the 600–650 cm<sup>-1</sup> range is shown. The  $\nu_4$  (ClO<sub>4</sub><sup>-</sup>) envelope can be separated in two contributions with the maximum at 625 and 636 cm<sup>-1</sup>. The 625 cm<sup>-1</sup> band to the spectroscopically free anions and the 635 cm<sup>-1</sup> mode to the bound or contact ClO<sub>4</sub><sup>-</sup> were confirmed by the fol-



**Figure 3** FTIR spectra of the ClO<sub>4</sub><sup>-</sup> absorbance for BTSE/PEG200 polymer electrolytes.



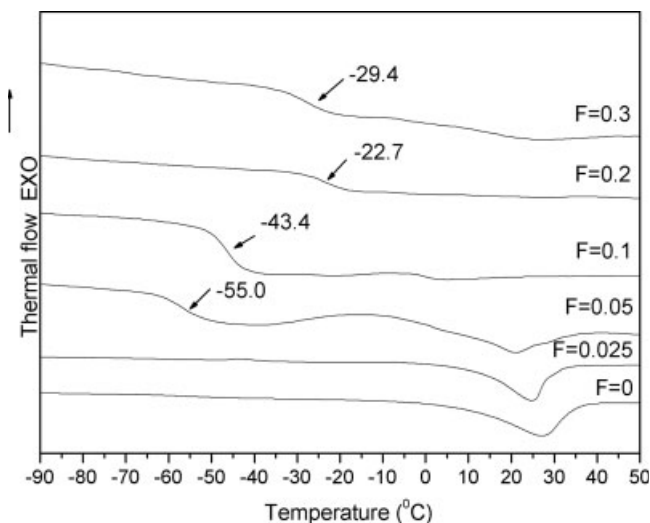
**Figure 4** Changes in the maximum of the C–O–C stretching for BTSE/PEG200 as a function of *F*.

lowing report.<sup>31</sup> The 625 cm<sup>-1</sup> constitutes the solvent-separated ionic clusters of –OH.....ClO<sub>4</sub><sup>-</sup>, the solvent-separated ion pairs of Li<sup>+</sup>.....ClO<sub>4</sub><sup>-</sup>, and the solvent-separated dimers of contact ion pairs. The bound ClO<sub>4</sub><sup>-</sup> consists mainly of contact ion pairs or aggregates.<sup>31</sup>

In Figure 4, the ratio of the area under the 625 cm<sup>-1</sup> mode to the total area under the ν<sub>4</sub> (ClO<sub>4</sub><sup>-</sup>) envelope is shown as a function of salt concentration for composite electrolytes. The fraction of free ions decreases with an increase in salt concentration up to *F* = 0.1, and then increases slightly for higher salt concentrations, attributed to the redissociation of free ions occurring at high salt concentrations.<sup>32</sup>

**Thermal analysis**

DSC was utilized to examine the effect of LiClO<sub>4</sub> on the thermal transitions of the BTSE-PEG-LiClO<sub>4</sub> com-



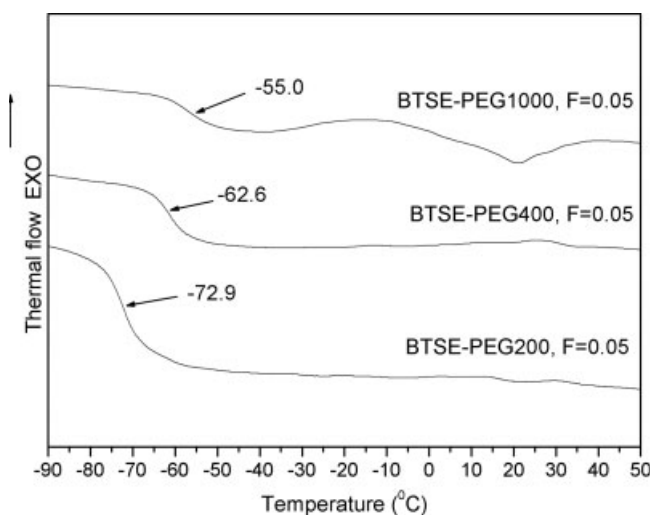
**Figure 5** DSC thermograms of the BTSE-PEG1000-LiClO<sub>4</sub> composite.

**TABLE I**  
Glass Transition Temperature (*T<sub>g</sub>*) (in °C) of the Composites

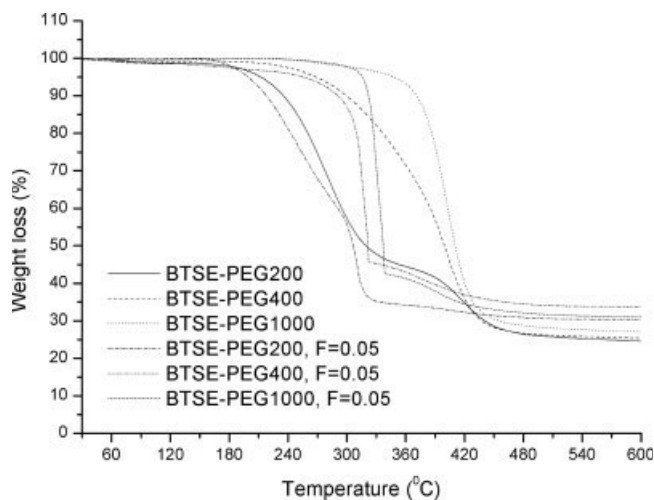
<i>F</i> (molar ratio)/sample	BTSE-PEG200	BTSE-PEG400	BTSE-PEG1000
0.025	-74.0	-65.0	-
0.05	-72.9	-62.6	-55.0
0.1	-58.2	-54.4	-43.4
0.2	-64.3	-56.7	-22.9
0.3	-55.7	-47.7	-29.4

posite electrolytes. Figure 5 shows the DSC thermograms of the BTSE-PEG1000-LiClO<sub>4</sub> composite electrolytes. It is seen that the thermogram varied with the *F* value. For the composite electrolytes with *F* ≤ 0.05, the heat capacity of the endotherm occurred at the melting temperature (around 23°C) indicating the destructure of ordering within the crystalline domains. *F* = 0.1 was reduced, with increase of the *F* value, the endotherm of the composite electrolyte is no longer discernible, but the glass transition is clearly seen. This phenomenon was not found in the PEG200 and PEG400 electrolyte systems, indicating that the structure of both is amorphous. As reported in Table I, the *T<sub>g</sub>* increased as the salt concentration increases and reaches a maximum salt temperature at *F* = 0.2, suggesting that the local motion of the polymer segments was retarded due to the formation of the transient crosslinks among the solvated lithium ions and the ethylene oxide segments of the polymer. The irregular variation of *T<sub>g</sub>* at higher salt concentration region may be attributed to the formation of ion pairs or ion clusters at high salt concentration, which reduced the ability to form ionic crosslinks.

Further more, Figure 6 shows that with the same salt content (*F* = 0.05), *T<sub>g</sub>* increases with the PEG



**Figure 6** DSC thermal curves of the BTSE-PEG-based composite polymer electrolytes with *F* = 0.05.



**Figure 7** TGA thermograms of the BTSE-PEG-based composite polymer electrolytes with  $F = 0.05$ .

chain length in the composite electrolytes, implying that more transient crosslinks were formed in the composite electrolyte with longer PEG chains. So, the low  $T_g$  of composite electrolyte results in low ionic conductivity as shown below.

Thermogravimetric analysis (TGA) was used to measure the thermal stability of the composite electrolytes. Figure 7 shows the weight loss behaviors of the undoped and  $\text{LiClO}_4$ -doped BTSE-PEG composite electrolytes, investigated by TGA scanning from 30 to 600°C under nitrogen. As can be seen,  $T_{5\%}$  of the undoped composite electrolytes, the temperature at which 5% weight is lost, was lower than that of  $\text{LiClO}_4$ -doped composite electrolytes. This is ascribed by the transient crosslinking, caused by the interaction of  $\text{Li}^+$  ions with the oxygen of the polymer matrix.<sup>33</sup> In addition, the  $T_{5\%}$  value was increased with an increase of PEG polymer chain.

### Ionic conductivity measurements

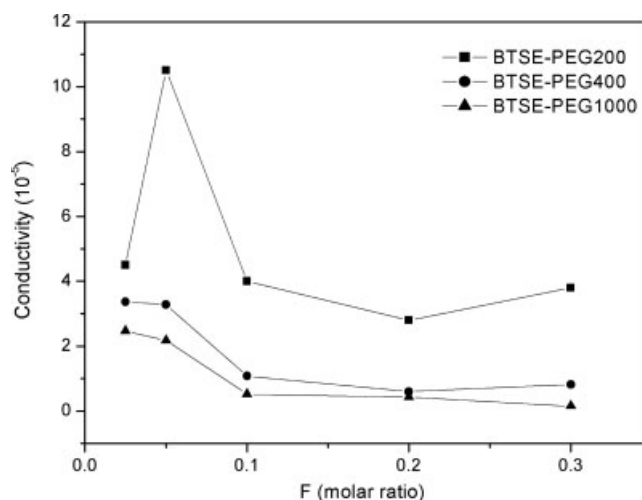
The ionic conductivities of all the composite electrolytes were determined by means of impedance spectroscopy using gold as blocking electrodes in the temperature range from 30 to 80°C. From the  $Z''$  versus  $Z'$  plot, ionic conductivity values were calculated at each temperature from the value intercept with the real axis.

The ionic conductivity data obtained as a function of  $\text{LiClO}_4$  concentration at 30°C are shown in Figure 8. It shows an increase in conductivity with  $\text{LiClO}_4$  salt concentration of  $F < 0.05$  and a maximum conductivity ( $1.4 \times 10^{-4} \text{ S/cm}$ ) at  $F = 0.05$  for the BTSE-PEG200 system. This result is similar to the maximum conductivity reported by Dahmouche et al.<sup>14</sup> for TEOS-PEG- $\text{LiClO}_4$  composite electrolytes. Following the maximum, the conductivity decreases for

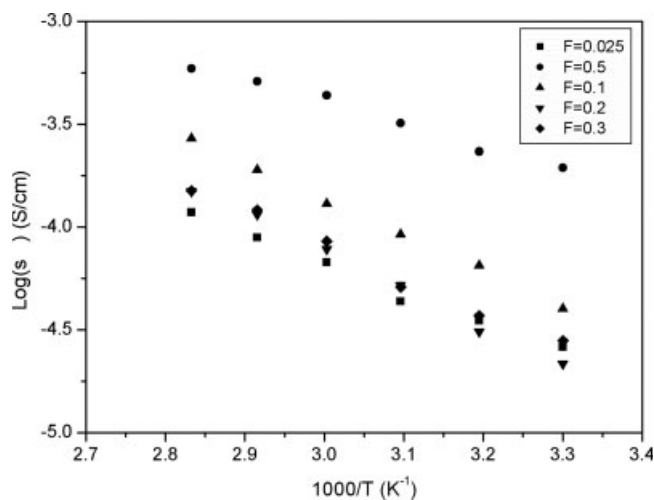
higher salt concentration. This is attributed to the reflection of two opposite effects, the increase in the number of charge carriers and the decrease in the free volume.<sup>34</sup> As the concentration of salt is increased, the number of charge carriers is also increased, but the average free volume is decreased due to the increase in  $T_g$  as discussed above. Hence, in the low concentration range, the conductivity mainly depends on the number of charge carriers. Hence, the conductivity is increased with an increase in salt concentration. When the salt concentration reaches the concentration of  $F = 0.05$  or more, the decrease in the free volume becomes more pronounced than the increase in the number of charge carriers. The lower fraction of free volume is no longer compensated by the continuous increase in the number of charge carriers. This results in decrease in conductivity with an increase in salt concentration at higher salt concentration range. Besides, the decrease in conductivity at higher salt concentration is also related to the formation of ion pairs and aggregates, which tend to favor with increasing salt concentration.

Figure 8 also shows the decrease of the conductivity as the PEG molecule weight was increased. The PEG chain mobility was decreased when the polymer chain length increased. Because of the absence of chemical bonds between the networks and the polymeric phase, which has a liquid-like behavior<sup>11,35</sup> with the configuration the interaction between the polymer chains themselves is less when the chains are short. Hence, their mobility is higher than that of long PEG chains.

Figure 9 shows the temperature dependence of ionic conductivity of the BTSE-PEG200- $\text{LiClO}_4$  composite electrolytes. The nonlinear dependence of conductivity with temperature can be best explained



**Figure 8** Change in conductivity of the BTSE-PEG- $\text{LiClO}_4$  composite polymer electrolytes with different salt concentrations.



**Figure 9** VTF plots of ionic conductivity of the BTSE-PEG200-LiClO<sub>4</sub> composite polymer electrolytes with different lithium salt concentrations.

with the Vogel–Tamman–Fulcher (VTF) relationship, where the transport of charge carrier is considered to be coupled with the segmental motion of the polymer host.

$$\sigma(T) = AT^{1/2} \exp[-B/k_b(T - T_0)]$$

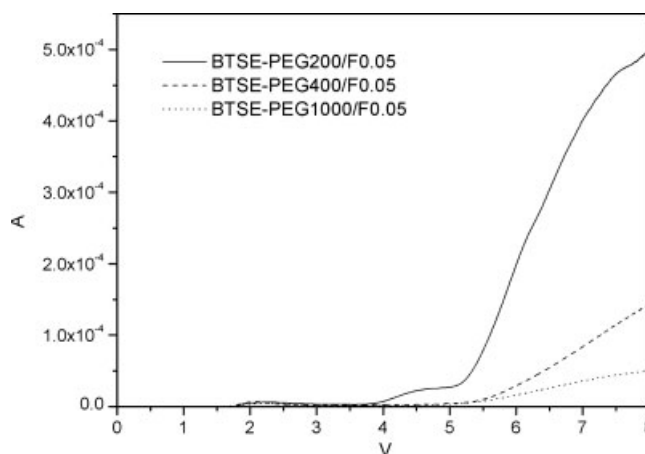
where  $A$  is a constant proportional to the number of carrier ions,  $B$  is the pseudo activation energy related to the polymer segmental motion,  $k_b$  is the Boltzmann constant, and  $T_0$  is a reference temperature at which the configurational entropy of the polymer becomes zero and is close to the glass transition temperature.

#### Transference number measurements

The transference number of lithium ( $t^+$ ) was calculated according the method reported.<sup>23</sup> The measurement is carried out on a symmetrical cell having nonblocking electrodes, where the composite electrolytes with different molecular weight were sandwiched between two lithium electrodes. As noticed in Table II, the  $t^+$  value decreased with decreasing polymer chain length, indicating that the highly resistive passivation layers were formed on lithium electrode.<sup>23</sup> The result suggests that the as-prepared

**TABLE II**  
Electrochemical Properties of the Samples  
(at  $F = 0.05$ ) at Room Temperature

Sample	$t^+$	Electrochemical stability window (V)
BTSE-PEG200	0.43	4.0
BTSE-PEG400	0.44	5.4
BTSE-PEG1000	0.48	5.5



**Figure 10** Linear sweeping voltammetry of BTSE/PEG/F0.05.

composite electrolyte with shorter PEG polymer chain contained much more residual —OH groups than that with longer PEG polymer chain, formed passivation layers more easily on the lithium electrodes.

#### Electrochemical stability window

An important parameter in the characterization of a given polymer electrolyte is the electrochemical stability window, especially in view of applications for lithium/polymer batteries. The parameter of the as-prepared composite electrolytes were determined by the linear sweep voltammetry on a cell containing the composite electrolyte sandwiched between a stainless steel working-electrode and a lithium counter-electrode. The potential of current onset may be regarded as the breakdown voltage of the electrolyte. Figure 10 shows the results for the BTSE-PEG-LiClO<sub>4</sub> composite electrolytes with different molecular weight of PEG. As seen, the potential window was above 4.0 V for all the samples, indicating that all the as-prepared composite electrolytes had an electrochemical stability window of at least 4.0 V. As listed in Table II, the voltammetry of electrochemical stability window increased with increasing PEG molecular weight. The PEG1000-containing composite electrolyte is up to about 5.5 V versus Li/Li<sup>+</sup>. In addition, the organosilica network acts as a stabilizer, enhancing the electrochemical stability of the PEG phase.

#### CONCLUSIONS

A new class of ionic conducting organic/inorganic hybrid composite electrolyte has been synthesized from ethylene-bridged polysilsesquioxane and poly(ethylene glycol) by the sol–gel process. The interpenetration of these two phases in the nanometer range shows that PEG chains are bonded and interact

to the silicon atoms to produce organosilica clusters, which could explain the polymeric behavior observed in the DSC measurements. The excellent phases lead to electrolytes with transparency, better thermal stability and mechanical behavior than for pure polymeric systems. The best conductivity obtained at the  $\text{LiClO}_4$  concentration of  $F = 0.05$  is up to  $1 \times 10^{-4}$  S/cm. The decrease of the conductivity as a function of the PEG chain length is found. The temperature dependence of conductivity of the composite electrolytes follows VTF equation in the temperature range of 30–80°C, implying the diffusion of charge carrier is assisted by the segmental motions of polymer chain. The cation transference number depends upon residual —OH formed from PEG polymer chain reacting with silanol groups.

## References

1. Maccallum, J. R.; Vincent, C. A. *Polymer Electrolyte Reviews*, vols. 1 and 2. Elsevier: London, 1987 and 1989.
2. Gray, F. M. *Solid Polymer Electrolytes—Fundamental and Technological Applications*; VCH: Weinheim, Germany, 1991.
3. Scrosati, B. *Applications of Electroactive Polymers*. Chapman And Hall: London, 1993.
4. Jiang, Z.; Carrol, B.; Abraham, K. M. *Electrochim Acta* 1997, 42, 2667.
5. Lightfoot, P.; Mehta, M. A.; Bruce, P. G. *J Mater Chem* 1992, 2, 139.
6. Boden, N.; Leng, S. A.; Ward, I. M. *Solid State Ionics* 1991, 45, 261.
7. Sanchez, J. Y.; Alloin, F.; Benrabah, D.; Arnaud R. *J Power Sources* 1997, 68, 43.
8. Judeinstein, P.; Sanchez, C. J. *Chem Mater* 1996, 6, 511.
9. Novak, B. M. *Adv Mater* 1993, 5, 422.
10. Ravaine, D.; Seminel, A.; Charbouillot, Y.; Vincens, M. *J Non-Cryst Solids* 1986, 82, 210.
11. Judeinstein, P.; Titman, J.; Stamm, M. *Schmidt Chem Mater* 1994, 6, 127.
12. Brik, M. E.; Titman, J. J.; Bayle, J. P.; Judeinstein, P. *J Polym Sci Part B: Polym Phys* 1996, 34, 2533.
13. Schmidt, H.; Poppal, M.; Rousseau, F.; Poinsignon, C.; Armand, M.; Rousseau, J. Y. *2nd Int Symp Polym Electrolytes* 1989, 325.
14. Dahmouche, K.; Atik, M.; Mello, N. C.; Bonagamba, T. J.; Panepucci, H.; Judeinstein, P.; Aegerter, M. A. *Sol Energy Mater Sol Cells* 1998, 54, 1.
15. Mello, N.; Bonagamba, T.; Panepucci, H.; Dahmouche, K.; Judeinstein, P.; Aegerter, M. *Macromolecules* 2000, 33, 1280.
16. Souza, P.; Bianchi, R.; Dahmouche, K.; Judeinstein, P.; Faria, R.; Bonagamba, T. *Chem Mater* 2001, 13, 3685.
17. Shea, K. J.; Loy, D. A. *Acc Chem Res* 2001, 34, 707.
18. Loy, D. A.; Shea, K. *J Chem Rev* 1995, 95, 1341.
19. Shea, K. J.; Joy, D. A.; Webster, O. W. *J Am Chem Soc* 1992, 114, 6700.
20. Barton, T. J.; Bull, L. M.; Klemperer, W.; Loy, G. D.; Mcenaney, A. B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem Mater* 1999, 11, 2633.
21. Cerveau, G.; Corriu, R.; Coord, P. *Chem Rev* 1998, 178–180, 1051.
22. Corriu, R. *Polyhedron* 1998, 17, 925.
23. Choe, H. S.; Carroll, B. G.; Pasquariello, D. M.; Abraham, K. M. *Chem Mater* 1997, 9, 369.
24. Yamanaka, S.; Sarubo, M.; Tadanobu, K.; Hattori, M. *Solid State Ionics* 1992, 57, 271.
25. James, D. W.; Mayes, R. E. *Aust J Chem* 1982, 35, 1775.
26. Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J Phys Chem Solids* 1981, 42, 493.
27. Eschmann, J.; Strasser, J.; Xu, M.; Okamoto, Y.; Eyring, E.; Petrucci, S. *J Phys Chem* 1990, 94, 3908.
28. Cohen, H. *J Chem Soc* 1952, 4282.
29. Liang, W. J.; Kuo, C. L.; Lin, C. L.; Kuo, P. L. *J Polym Sci Polym Chem Ed* 2002, 40, 1226.
30. Bruce, P. G. *Solid State Electrochemistry*, 1995.
31. Salomon, M.; Xu, M.; Eyring, E. M.; Petrucci, S. *J Phys Chem* 1994, 98, 8234.
32. Petrucci, S.; Eyring, E. M. *J Phys Chem* 1991, 95, 1731.
33. Kuo, P. L.; Liang, W. J.; Chen, T. Y. *Polymer* 2003, 44, 2957.
34. Digar, M.; Hung, S. L.; Wang, H. L.; Wen, T. C.; Gopalan, A. *Polymer* 2002, 43, 681.
35. Judeinstein, P.; Brik, M. E.; Bayle, J. P.; Courtieu, J.; Rault, J. *MRS Symposium Proc* 1994, 346, 937.