

X. J. Wang · H. P. Zhang · J. J. Kang  
Y. P. Wu · S. B. Fang

## Novel composite polymer electrolytes based on poly(ether-urethane) network polymer and fumed silicas

Received: 7 January 2005 / Revised: 8 March 2005 / Accepted: 6 June 2005 / Published online: 21 October 2005  
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**Abstract** Novel composite solid polymer electrolytes (CSPEs) and composite gel polymer electrolytes (CGPEs) have been prepared. CSPE consists of poly(ether-urethane) network polymer (PUN), fumed silicas and  $\text{LiClO}_4$ . The ionic conductivity of CSPEs can be enhanced nearly 20 times in comparison with the plain system without the addition of fumed silicas and can be above  $1 \times 10^{-5}$  S/cm at room temperature. The effects of both kinds of fumed silicas, viz.  $\text{uSiO}_2$  with hydrophilic groups at the surface and  $\text{mSiO}_2$  with hydrophobic groups at the surface on ionic conductivity were investigated. CGPE comprising of the CSPE and  $\text{LiClO}_4$ -PC solution with good mechanical strength exhibits ionic conductivity in the order of  $10^{-3}$  S/cm at room temperature and above  $3 \times 10^{-4}$  S/cm at low temperature  $-40$  °C.

room temperature ( $\sigma < 10^{-5}$  S/cm) and poor mechanical properties due to the high crystallization degree of PEO [3, 4].

One of the methods to obtain a PEO-based polymer electrolyte with high ionic conductivity is to prepare composite solid polymer electrolyte (CSPE) by adding fine fillers [2, 5, 6]. It was reported that the addition of  $\alpha$ - $\text{Al}_2\text{O}_3$  powder,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\gamma$ - $\text{LiAlO}_2$  results in improved mechanical properties, an increase in cation transference number and ionic conductivity at low-temperature of PEO-based polymer electrolytes, and an improved interfacial stability between the CSPEs and the lithium metal electrode [5–8].

Recently, fumed silica got considerable interests to prepare CSPE [9–11] because fumed silica has several distinct advantages [12], i.e., (1) its “starburst” particulate shape helps to reduce the crystallinity of the host polymer at low solid loading; (2) its large surface area leads to an open network structure supporting high ionic mobility; (3) its surface groups can be modified to meet a specific need. As a result, after the addition of treated  $\text{SiO}_2$  powders, the ionic conductivity of poly(ethylene glycol) (PEG)-based CSPE could be enhanced five to tenfolds [9]. For CSPE based on the fumed silica and PEG of low molecular weight, gel-like electrolytes were produced due to the formation of a network structure via physical cross-linking provided by the fumed silica, and these electrolytes achieve ionic conductivity at room temperature exceeding  $10^{-3}$  S/cm [13, 14]. In such gel, the number of combination points will change upon variation of the external conditions such as temperature, concentration, or stress, because the gel network is formed via physical crosslinking [2]. For CSPEs based on fumed silica and the linear PEO with high molecular weight [10, 12, 15], the room temperature conductivity continues to be a limiting factor. The swelling of such CSPE by liquid electrolyte can also achieve high ionic conductivity at room temperature. However, poor mechanical properties will still be encountered with, and thus the linear structure of the PEO hinders the application of such CGPE in rechargeable lithium batteries.

### Introduction

Solid polymer electrolytes (SPEs) have received considerable attention for their potential application as electrolytes in modern electronics ever since the discovery of the polymer electrolytes based on poly(ethylene oxide) (PEO) [1, 2]. PEO-based polymer electrolytes have been extensively studied because of their beneficial structure in supporting fast ion transport. These systems, however, still suffer from inadequate ionic conductivity at

X. J. Wang · H. P. Zhang · Y. P. Wu (✉)  
Department of Chemistry Shanghai Key Laboratory  
of Molecular Catalysis and Innovative Materials,  
Fudan University, Shanghai, 200433, China  
E-mail: wuyyp@fudan.edu.cn  
Tel.: +81-21-55664223  
Fax: +86-21-55664223

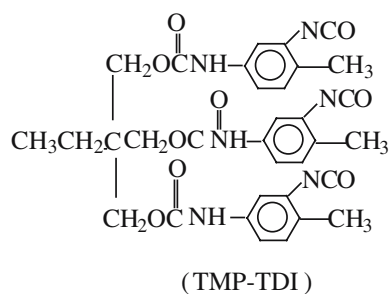
J. J. Kang · S. B. Fang · Y. P. Wu  
Institute of Chemistry, Chinese Academy of Sciences,  
Beijing, 100080, China

The formation of network via chemical crosslinking is an interesting way to obtain polymer complex with high ionic conductivity in combination with good processability, mechanical strength and dimensional stability at relatively high temperature and under pressure [16–19]. In addition, this kind of network structure also helps to trap the liquid electrolyte within the polymer matrix [18–20].

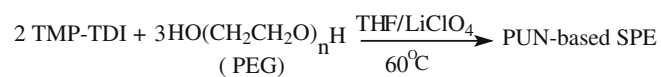
In this paper, CSPE based on poly(ether-urethane) network polymer (PUN) from chemical crosslinking reaction of PEG with a crosslinker were reported. Two kinds of fumed silicas, mSiO<sub>2</sub> with hydrophobic groups at the surface and uSiO<sub>2</sub> with hydrophilic groups at the surface, were used as fillers. Effects of these two fillers on the crystallinity and ionic conductivity were primarily investigated. In addition, composite gel polymer electrolytes (CGPEs) were prepared by dipping the dry CSPE films in a liquid electrolyte.

## Experimental

The crosslinking agent (TMP-TDI) with three NCO groups was synthesized in our laboratory [18, 19] and its chemical structure is shown below:

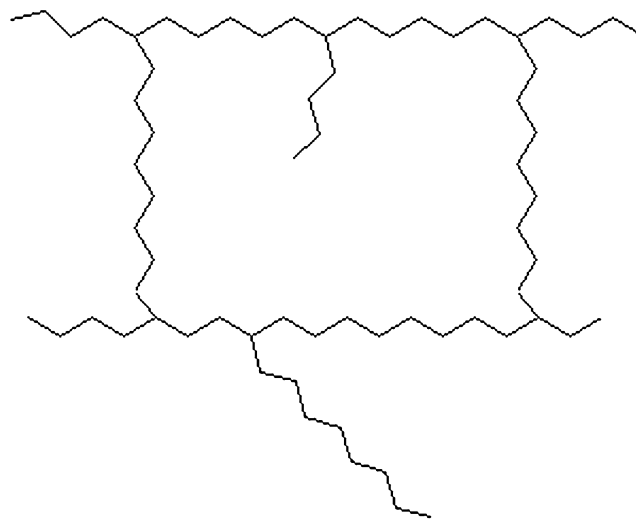


The fumed silicas, mSiO<sub>2</sub> of average particle size 12 nm with hydrophobic groups at the surface and uSiO<sub>2</sub> of average particle size 20 nm with the native hydroxyl groups at the surface, were kindly provided by High-Tech Materials Laboratory of our institute. PUN-based solid polymer electrolyte (SPE) was synthesized according to Scheme 1, whose structure is schematically shown in Fig. 1. Since the crosslinking could not be 100%, there are some pentant groups or side chains.



**Scheme 1** Preparation of PUN-based solid polymer electrolyte

An equivalent amount of PEG with an average molecular weight 1,000 and the crosslinker TMP-TDI were dissolved in anhydrous tetrahydrofuran (THF) in a flask equipped with a condenser and then an appropriate



**Fig. 1** Schematic structure of PUN-based solid polymer electrolyte (SPE) according to Scheme 1

amount of dried LiClO<sub>4</sub> ([EO]/[Li] = 12.5) was added to the above solution. With vigorous stirring, the solution was heated at 60 °C for 1 h. The obtained viscous solution was then cast onto a square PTFE mold, which was put on an exact horizontal plane. After curing in a vacuum oven at 80 °C for 48 h, the final product, SPE, was obtained. The preparation procedure of CSPE was similar to that of SPE except the addition of the fumed silicas before heating the solution.

For the preparation of CGPEs, SPE and CSPE films with accurately known weights were immersed in a liquid electrolyte [1.5 M LiClO<sub>4</sub> in propylene carbonate (PC)]. The liquid electrolyte was prepared by dissolving vacuum dried anhydrous LiClO<sub>4</sub> in PC from vacuum distillation in the presence of sodium. The swelling processes were carried out at room temperature. The dipped films were taken out from the liquid electrolytes at different times, and their weights, thickness, diameter and ionic conductivities were measured. The solution contents (SC) in the films were determined:

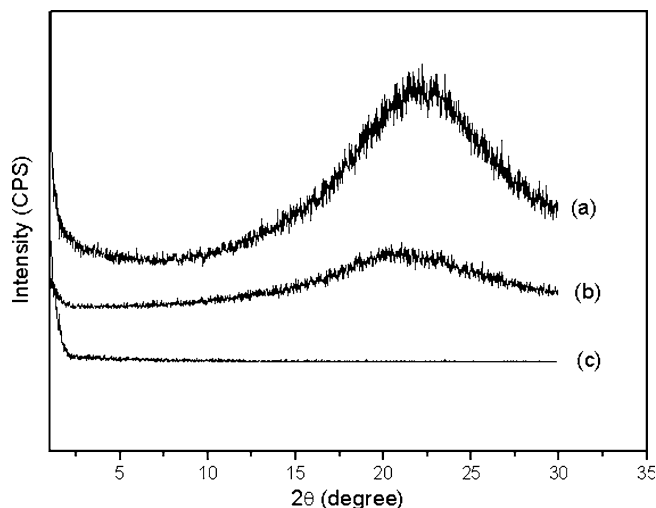
$$\text{SC}(\%) = (W_t - W_0) / W_t \times 100\%, \quad (1)$$

where  $W_0$  and  $W_t$  are the weights of the dry and the swelled films, respectively.

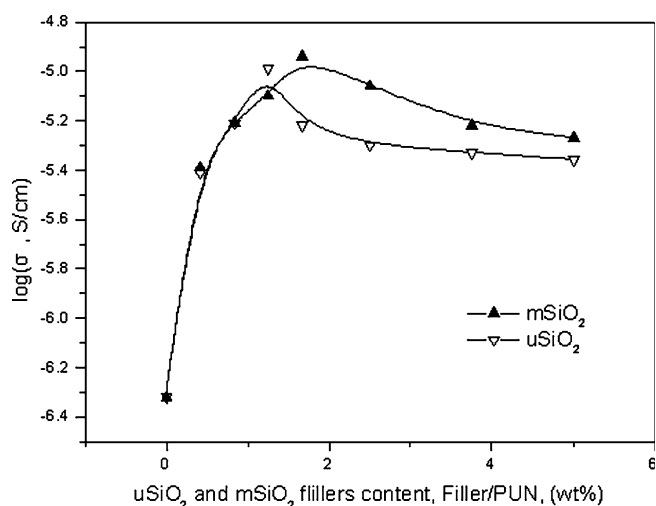
The ionic conductivity was measured using HIOKI LCR 3520 HI TESTER at 1 kHz, and the film was placed in a Teflon spacer ring, compressed between two stainless steel electrodes, and sealed in a testing cell. X-ray diffraction (XRD) patterns were recorded with an X-ray diffraction meter (Rigaku D/max-2500) in the range of  $2\theta = 1\text{--}30^\circ$ .

## Results and discussion

The XRD patterns corresponding to pristine SPE, uSiO<sub>2</sub>-added CSPE and mSiO<sub>2</sub>-added one, are shown in



**Fig. 2** XRD patterns of **a** pristine PUN/LiClO<sub>4</sub> SPE, **b** PUN/uSiO<sub>2</sub>/LiClO<sub>4</sub> CSPE (the amount of uSiO<sub>2</sub> based on PUN is 1.25 wt%), and **c** PUN/mSiO<sub>2</sub>/LiClO<sub>4</sub> CSPE (the amount of mSiO<sub>2</sub> based on PUN is 1.67 wt%)



**Fig. 3** Ionic conductivity versus the addition amount uSiO<sub>2</sub> and mSiO<sub>2</sub> fillers for PUN/filler/LiClO<sub>4</sub> CSPEs at 30 °C ([EO]/[Li]=12.5)

**Fig. 2.** In Fig. 2a, the XRD pattern of pristine SPE shows one crystalline peak at about 22.5 °. The intensity of the crystalline peak decreased obviously when fumed silica fillers were added as shown in Fig. 2b and c. This indicates that the crystallinity of the PUN-based SPE can be reduced by the added fillers, and the mSiO<sub>2</sub> is more effective in decreasing the crystallinity of the SPE than the uSiO<sub>2</sub>.

Dependence of ionic conductivities at 30 °C on the content of the fillers is illustrated in Fig. 3. It shows that two curves have the same general character. The ionic conductivity initially increases and attains a maximum when the amounts of mSiO<sub>2</sub> and uSiO<sub>2</sub> based on PUN arrive at about 1.67 and 1.25 wt%, respectively. The

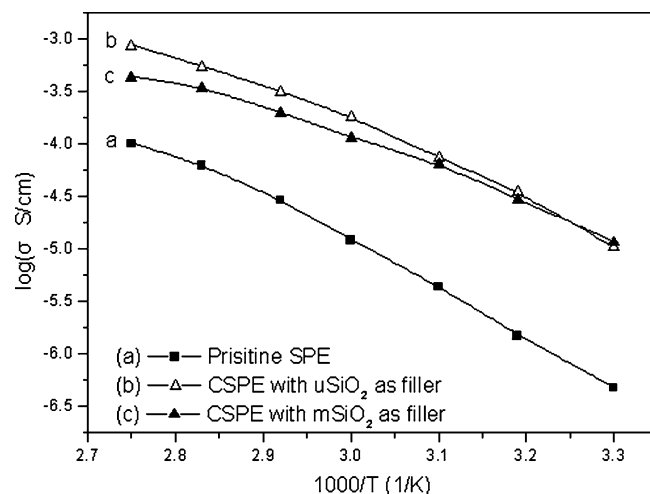
presence of the fumed silicas induce an enhancement of the conductivity of about 20 times, from  $4.83 \times 10^{-7}$  S/cm to  $1.15 \times 10^{-5}$  S/cm, and  $1.02 \times 10^{-5}$  S/cm, respectively. After the maximum conductivity is reached, the ionic conductivity decreases with the content of the fillers.

Conductivity ( $\sigma$ ) is determined by ionic mobility ( $\mu$ ), carrier number ( $n$ ), and charge ( $q$ ) as the following Eq. (2):

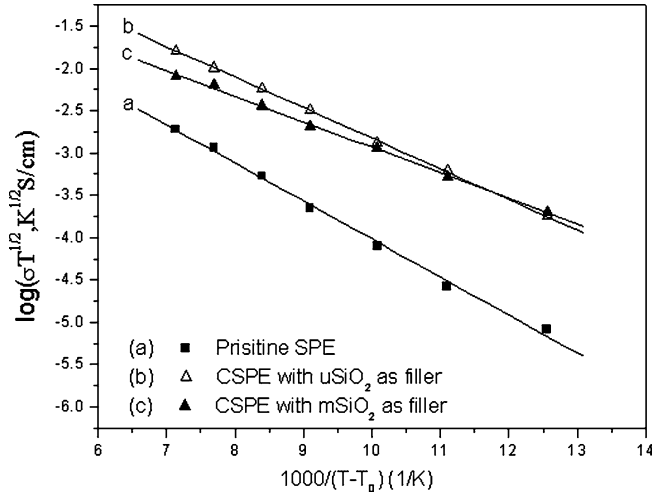
$$\sigma = \sum \mu n q. \quad (2)$$

For the present CSPE, charge is constant, so the reason for the maximum behavior of the ion conductivity could be related to the change in mobility and number of charge carriers after the addition of the fillers. It is known that ionic mobility is intimately connected with the segmental motion of the polymer chains. When the addition amounts of the fillers are low, the crystallization of the CSPE is suppressed as shown in Fig. 2, so the polymer can move more easily and the free volume increases. The charge carriers can move into the free volume, leading to an increase in ionic conductivity. At higher filler contents, continuous non-conductive phase built up by the fillers would block transport of lithium ions, resulting in the decrease of conductivity of the CSPE [21]. The enhancement of the ionic conductivity in these composite systems may also be related to the change in the number of charge carriers caused by the interaction between the silica and the polymer electrolyte, as discussed in the following.

Figure 4 illustrates the temperature dependence of the conductivity for the mSiO<sub>2</sub>- and uSiO<sub>2</sub>-added composite PUN-LiClO<sub>4</sub>-based electrolytes in comparison with that of filler-free polymer electrolyte. It is evident that the plots of  $\log \sigma$  versus  $1/T$  are curved rather than linear, which suggest that lithium transport occurs in



**Fig. 4** Temperature dependence of the ionic conductivity for **a** pristine PUN/LiClO<sub>4</sub> SPE, **b** PUN/uSiO<sub>2</sub>/LiClO<sub>4</sub> CSPE (the amount of uSiO<sub>2</sub> based on PUN is 1.25 wt%), and **c** PUN/mSiO<sub>2</sub>/LiClO<sub>4</sub> CSPE (the amount of mSiO<sub>2</sub> based on PUN is 1.67 wt%)



**Fig. 5** Vogel-Tammann-Fulcher plots of ionic conductivity for **a** pristine PUN/LiClO<sub>4</sub> SPE, **b** PUN/uSiO<sub>2</sub>/LiClO<sub>4</sub> CSPE (the amount of uSiO<sub>2</sub> based on PUN is 1.25 wt%), and **c** PUN/mSiO<sub>2</sub>/LiClO<sub>4</sub> CSPE (the amount of mSiO<sub>2</sub> based on PUN is 1.67 wt%)

amorphous region, and the ionic conduction follows Vogel-Tammann-Fulcher (VTF) equation [22–24].

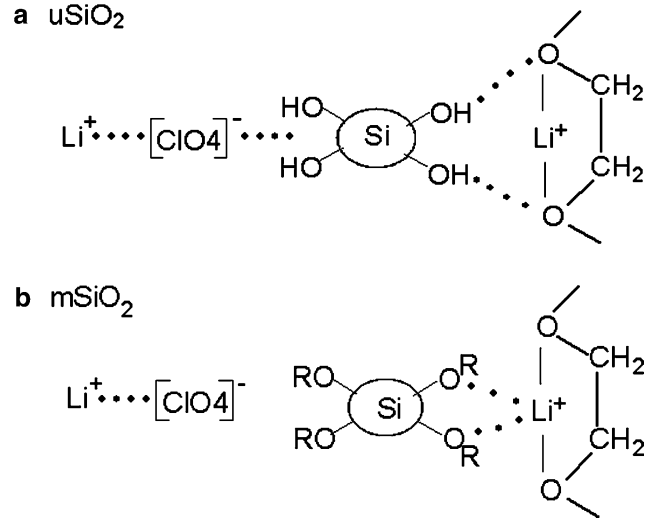
$$\sigma = \frac{A}{T^{1/2}} e^{-E_a/R(T-T_0)}, \quad (3)$$

where  $A$  and  $E_a$  are constants. The former is related to the number of charge carriers, and  $E_a$  is the activation energy for ionic conduction.  $T$  is the measured temperature in the unit of K and  $T_0$  is a temperature related to  $T_g$ . According to Gibbs configuration entropy model,  $T_0$  is regarded as 50 K below the measured  $T_g$  [25].  $T_g$  is the same as that of PEO, which is well known to be 223 K (−50 °C). As a result,  $T_0$  is 173 K. The results of the fitting are shown in Fig. 5. From plots  $\log(\sigma T^{-1/2})$  versus  $1/(T-T_0)$ , well-fitted straight lines are observed. This indicates that the process of ion conduction is closely related to the polymer segmental motion. The fitted parameters  $A$  and  $E_a$  are calculated and shown in Table 1. It presents that the activation energy  $E_a$  decreases after the addition of uSiO<sub>2</sub> and mSiO<sub>2</sub>, which suggests that lithium ions can transport more easily. This is consistent with the above results from X-ray diffraction, the amounts of amorphous phase in both composite systems are increased upon the addition of the fillers.

It is well known that our small molecule PEG (MW = 1000) can be used as a plasticizer for solid polymer electrolytes. The activation energy for the movement of lithium ion is very low, similar to the

behavior in liquid electrolyte, about several kJ/mol. In our synthesized cross-linked polymers, the structure could not be very perfect and there are some residual pendant groups of  $-(\text{CH}_2\text{OCH}_2\text{O})_n-\text{OH}$ . As a result, it is lower than that of normal solid polymer electrolytes.

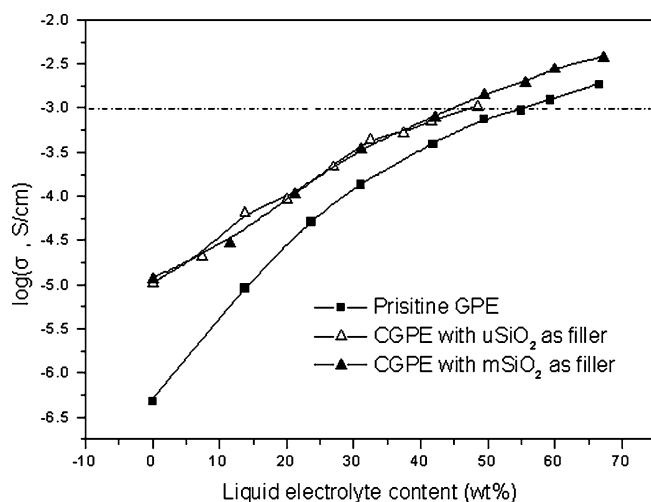
For comparison, Table 1 also shows that the pre-exponential factor  $A$  for the uSiO<sub>2</sub>-added CSPE (0.97) is higher than that of the filler-free SPE (0.29), and that for the mSiO<sub>2</sub>-added CSPE (0.26) is almost the same as that of filler-free SPE. From these results, it is evident that the conductivity enhancement in the uSiO<sub>2</sub>-added CSPE cannot solely be attributed to the increase of amorphous phase, it is also related to specific interactions induced via Lewis acid–base reaction between the filler’s surface and the polymer electrolyte. Indeed, the occurrence of specific interactions between added ceramic fillers and polymer electrolytes has been suggested [7, 8] and supported by the results from X-ray energy dispersive analysis for CSPE of P(EO)<sub>8</sub>LiClO<sub>4</sub> and 10 wt% TiO<sub>2</sub> and Raman spectroscopy [8, 26]. The TiO<sub>2</sub> powders influence ion aggregation in amorphous CSPEs by promoting TiO<sub>2</sub>-salt interactions. The interaction between the silica and lithium ions is also studied by the solid <sup>7</sup>Li NMR spectroscopy [27]. The expected interactions between the fumed silica and the polymer electrolyte in our two prepared CSPEs are suggested in Fig. 6 [28]. For the uSiO<sub>2</sub>-added CSPE, the filler can



**Fig. 6** Pictorial model of the surface interaction between two forms of dispersed fumed silica filler and the PUN-LiClO<sub>4</sub> electrolyte complex: **a** uSiO<sub>2</sub> with the native hydroxyl groups at the surface; **b** mSiO<sub>2</sub> with hydrophobic groups R at the surface

**Table 1** Ionic conductivity and VTF parameters for the SPE and CSPEs

Type of SPE	$\sigma$ (30 °C) (S/cm)	$\sigma$ (80 °C) (S/cm)	$A$ (K <sup>1/2</sup> S/cm)	$E_a$ (kJ/mol)
Pristine SPE	$4.8310^{-7}$	$6.05 \times 10^{-5}$	0.29	5.04
CSPE (uSiO <sub>2</sub> added)	$1.02 \times 10^{-5}$	$5.42 \times 10^{-4}$	0.97	4.05
CSPE (mSiO <sub>2</sub> added)	$1.15 \times 10^{-5}$	$3.35 \times 10^{-4}$	0.26	3.43



**Fig. 7** Dependence of the ionic conductivity for SPE from PUN/LiClO<sub>4</sub> and CSPEs from PUN/filler/LiClO<sub>4</sub> (the amount of uSiO<sub>2</sub> and mSiO<sub>2</sub> based on PUN is 1.25 and 1.67 wt%, respectively) on the content of 1.5 M LiClO<sub>4</sub> solution in PC

provide hydrogen bonds with the salt anions as well as with oxygen of the PEO chains, which is consistent with the results from X-ray diffraction that the CSPE based on uSiO<sub>2</sub> still presents some kind of crystal phase. In contrast, in the case of mSiO<sub>2</sub> filler only ion-dipole interactions are expected and almost completely amorphous phase is achieved, therefore the uSiO<sub>2</sub> filler is expected to be a little more efficient in promoting salt dissociation and freeing lithium ions from the coordination with PEO chains than the mSiO<sub>2</sub> filler, resulting in the increase of the charge carrier number.

Based on the above results, as for uSiO<sub>2</sub>-added CSPE, it is possible to assume that the increase in conductivity of CSPE is attributed to the enhancement in the amount of the amorphous phase (favoring the increase of the ion mobility) as well as to the Lewis acid-base type ceramic-electrolyte interactions (favoring the increase of the number of charge carriers). While in the case of mSiO<sub>2</sub>-added CSPE, the increase in conductivity may be attributed mostly to the former. However, the degree is different. At 30 °C, the ionic conductivity of the uSiO<sub>2</sub>-added CSPE is lower than that of the mSiO<sub>2</sub>-added one, which seems to indicate that ion mobility (related to the degree of the amorphous phase in the composite system) plays a predominant role in influencing the ionic conductivity. At higher temperature (above 40 °C), the ionic conductivity of the uSiO<sub>2</sub>-added CSPE is higher than that of the mSiO<sub>2</sub>-added one, and the number of charge carriers plays a more predominant role in influencing the ionic conductivity.

Figure 7 shows the dependence of ionic conductivity of GPE and CGPEs systems at room temperature on the content of PC-LiClO<sub>4</sub> solution. Comparison of the CGPEs with the pristine one also shows an increase in conductivity. These two CGPEs have almost the same ionic conductivity at certain content of the PC-LiClO<sub>4</sub>

solution. The CGPE with desired conductivity of 10<sup>-3</sup> S/cm can be obtained when the content of the PC-LiClO<sub>4</sub> solution is about 50 wt% at room temperature.

At low temperature -40 °C, the ionic conductivity of mSiO<sub>2</sub>- and uSiO<sub>2</sub>-added CGPEs with 66 wt% PC-LiClO<sub>4</sub> solution is 3.65×10<sup>-4</sup> S/cm and 6.69×10<sup>-4</sup> S/cm, respectively, remaining at satisfactory level. This primary result suggests that this kind of CGPE is also possible for low temperature application.

## Conclusion

Two novel types of CSPEs composed of chemical crosslinked poly(ether-urethane), fumed silicas, and LiClO<sub>4</sub> were prepared. This study demonstrates that the addition of fumed silicas can suppress the crystallinity of CSPEs, and increase the ion conductivity by 20 times exceeding 10<sup>-5</sup> S/cm. The temperature dependence of conductivity of the CSPEs follows VTF equation in the temperature range of 30–90 °C. The increase in ionic conductivity of the uSiO<sub>2</sub> (with hydrophilic surface groups)-based CSPE is attributed to the enhancement of degree of the amorphous phase as well as to some Lewis acid-base type ceramic-electrolyte interactions, and the increase in ionic conductivity of the mSiO<sub>2</sub> (with hydrophobic surface groups)-based one is mostly attributed to the former. CGPEs comprising of the CSPEs and 1.5 M LiClO<sub>4</sub> solution in PC with good mechanical strength exhibit ionic conductivity in the order of 10<sup>-3</sup> S/cm at room temperature and satisfactory level at -40 °C, providing promise for their application in polymer lithium ion batteries.

**Acknowledgements** We gratefully acknowledge the financial supports of the National High Technology Research and Development Program ("863" Research Project) (No. 2001AA320304) & China Natural Sciences Foundation (No: 20333040).

## References

- Gray FM (1991) Solid polymer electrolytes: fundamentals and technological applications. VCH Publishers, New York
- Wu YP, Wan C, Jiang C, SB Fang (2002) Lithium ion secondary batteries. Chemical Industry Press, Beijing
- Feton DE, Parker JM, Wright PV (1973) Polymer 14:589
- Fauteux D, Massucco AA, Buren MV, Shi J (1995) Electrochim Acta 40:2185
- Quartarone E, Mustarelli P, Magistris A (1998) Solid State Ionics 110:1
- Weston JE, Steele BC (1982) Solid State Ionics 7:75
- Croce F, Appetecchi GB, Persi L, Scrosati B (1998) Nature 394:456
- Croce F, Curini R, Martinello A, Persi L, Ronci F, Scrosati B, Caminiti R (1999) J Phys Chem 103:10632
- Matsuo Y, Kuwano J (1995) Solid State Ionics 79:295
- Capiglia C, Mustarelli P, Quartarone E, Tomasi C, Magistris A (1999) Solid State Ionics 118:73
- Walls J, Zhou J, Yerian JA, Fedkiw PS, Khan SA, Stowe MK, Baker GL (2000) J Power Sources 89:156
- Liu Y, Lee JY, Hong L (2002) J Power Sources 109:507
- Fan J, Fedkiw PS (1997) J Electrochem Soc 144:399

14. Raghavan SR, Riley MW, Fedkiw PS, Khan SA (1998) *Chem Mater* 10:224
15. Scrosati B, Croce F, Persi L (2000) *J Electrochem Soc* 147:1718
16. Kim JY, Kim SH (1999) *Solid State Ionics* 124:91
17. MacDallum JR, Smith MJ, Vincent CA (1984) *Solid State Ionics* 11:307
18. Zhang ZC, Fang SB (2000) *J Appl Polymer Sci* 77:2957
19. Wang XJ, Kang JJ, Wu YP, Fang SB (2003) *Electrochem Commun* 5:1025
20. Borghini MC, Mastragostino M, Zanelli A (1996) *Electrochim Acta* 41:2369
21. Itoh T, Ichikawa Y, Uno T, Tubo M, Yamamoto O (2003) *Solid State Ionics* 156:393
22. Vogel H (1921) *Phys Z* 22:645
23. Tamman V, Hesse W (1926) *Allg Chem* 156:245
24. Fulcher G (1925) *J Am Chem Soc* 8:339
25. Adam G, Gibbs JH (1965) *J Chem Phys* 43:139
26. Best AS, Ferry A, MacFarlane DR, M Foesyth (1999) *Solid State Ionics* 126:269
27. Lee KH, Lee YG, Park JK, Seung DY (2000) *Solid State Ionics* 133:257
28. Croce F, Persi L, B Scrosati, Fiory FS, E Plichta, Hendrickson MA (2001) *Electrochim Acta* 46:2457