

Combined effects of ceramic filler size and ethylene oxide length on the ionic transport properties of solid polymer electrolyte derivatives of PEGMEMA

Fu-Ming Wang · Ju-Hsiang Cheng · Bing-Joe Hwang · Raman Santhanam

Received: 1 December 2010 / Revised: 29 December 2010 / Accepted: 30 December 2010 / Published online: 26 January 2011
© Springer-Verlag 2011

Abstract In this work, the synthesis of a series of solid polymer electrolyte (SPE) derivatives of poly(ethylene glycol) methyl ether methacrylate (PEGMEMA), homogeneously dispersed with TiO₂ ceramic nano-filler, has been reported. The interactions between filler size and the length of the ethylene oxide (EO) polymer backbone are discussed, and transport properties such as ionic conductivity and cation transference number are determined. Results show that the improved performance of the SPE is due to an interaction between the ceramic filler and the entwining behavior of the PEGMEMA backbone. An optimal ceramic filler size and an appropriate length of EO have been suggested for the enhanced performance of SPE derivatives of PEGMEMA for a next-generation polymer battery.

Keywords Solid polymer electrolyte · Filler · Ionic transport · Ethylene oxide · Polyacrylate

Introduction

The development of solid polymer electrolytes (SPEs) has received much attention during the last 25 years because they are non-volatile and non-toxic, easy to manufacture, stable under high-voltage operation, and have no leakage problem [1–3]. The ionic transfer mechanism and ionic pathway of SPEs and liquid carbonate electrolytes are entirely different [4–6] due to the carbonate liquid electrolyte providing the lithium salts which are completely dissociated to single lithium ions by the unsymmetrical linear carbonate structure and dielectric constant; therefore, the transference number and diffusion coefficient of the cations show that the lithium ions are important and dominate the ionic transfer and the passivation layer properties and relate to battery performance. However, the parameters of cation mobility in solid polymer electrolytes were increased by increasing the lengths of the ethylene oxide (EO) side chain and other flexible backbone structures. Therefore, the cation mobility in polymer structures is quite different compared to liquid-based systems and is probably suppressed, resulting in their polymer structure. According to previously published results [7, 8], the polymer's electron-withdrawing groups cause differences in Van der Waals force interactions and thus influencing an ion transport "hopping" mode. Additionally, free volume and chain flexibility in the bulk polymer decide whether or not the hopping ionic transport mode is available. Cationic and anionic volumes, following salt dissociation, affect ionic transport velocity. Thus, several factors require consideration when selecting a suitable polymer to prepare an SPE. Any new type of SPE should have a low glass transition temperature, high

F.-M. Wang (✉)
Nanoelectrochemistry Laboratory, Graduate Institute
of Engineering, National Taiwan University of Science
and Technology,
Taipei, Taiwan
e-mail: mccabe@mail.ntust.edu.tw

J.-H. Cheng · B.-J. Hwang
Nanoelectrochemistry Laboratory, Department of Chemical
Engineering, National Taiwan University of Science
and Technology,
Taipei, Taiwan

R. Santhanam
Enerdel Inc.,
Indianapolis, IN, USA

free volume, and highly flexible backbone for facile ionic transfer. SPEs do not offer the same performances as the liquid carbonate electrolytes due to the low ionic conductivity of crystalline polymers. Different research groups report various strategies in order to reduce the problems associated with SPEs and optimize their properties, including the use of phase exchange block copolymers [9, 10] and nano-grade metal oxide addition [11, 12], to eliminate the degree of crystallization. Other reported methods for improving SPE performance include the addition of hyper-branched oligomers to increase whole polymer free volume [6] and the direct synthesis of novel SPE polymer with a soft backbone [13]. Considering the economic efficiency, the use of nano-metal oxide particles offers the possibility of commercial development of SPE with a stable conducting polymer and simple fabrication method. According to the literatures, thin film battery [14], separator free battery [15], and flexible battery [16] applications with low elastic moduli of SPE or gel polymer electrolyte are going to be used and designed by spin coating or doctor blade casting in the next-generation polymer lithium ion battery.

Liu et al. studied the effect of SiO₂ particles, prepared by using different methods, on the transport properties of the polymer electrolytes [11]. Their results indicate that SiO₂, synthesized by in situ sol–gel method, provides the hydroxyl functional group which can form hydrogen bonds with EO and hence increase the intermolecular distances and polymer free volume within the SPE. This improvement relatively enhances the SPE cation transference number when compared to that of conventional poly(ethylene oxide) (PEO) electrolytes. Hwang et al. studied the effects of nano-sized TiO₂ particles on the ionic transport properties of bulk polymer electrolytes. In the above study, the interactions between particle and bulk polymer were investigated by dispersing various nano-sized (3.7, 6.2, and 22 nm) TiO₂ particles with PEO [12]. Unfortunately, Hwang's report did not identify any comprehensive relationship between particle size and ionic transfer properties such as ionic conductivity and transfer number. Although some reports indicate that smaller metal oxide particles significantly assist ionic transfer [17, 18], only a few papers are concerned with the fundamental interaction between EO side chain length and particle size [12, 19].

The aim of the present work is to contribute to the better understanding of the combined role of various ceramic filler particle sizes and the length of EO chain. For that, the ceramic particles with different sizes were dispersed into solid polymer electrolyte derivatives of poly(ethylene glycol)methyl ether methacrylate (PEGMEMA) with different EO chain length and the improvement in the transport properties is discussed with a possible explanation.

Experimental

Materials

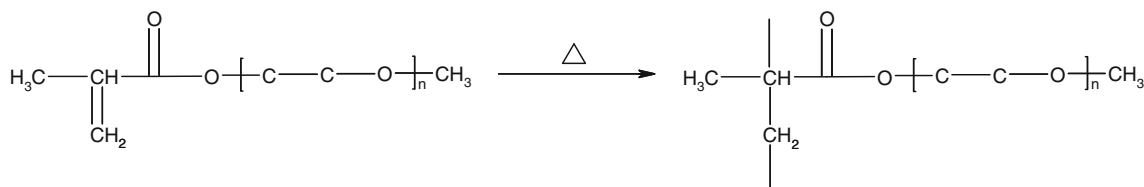
Poly(ethylene glycol) methyl ether methacrylate ($M_n=300$, 475, and 1,100) and titanium (IV) oxide (anatase, 5 and 25 nm) were purchased from Sigma-Aldrich Chemicals. All of the polymers were dried over molecular sieves prior to use. The initiator, di(4-tert-butylcyclohexyl)peroxydicarbonate (BCHPC), was supplied by Showa. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSi) was obtained from 3M Co. The repeat unit of PEO on PEGMEMA₃₀₀, PEGMEMA₄₇₅, and PEGMEMA_{1,100} are measured to 4~5, 8~9, and 20~21 by computer calculation.

Preparation of composite solid polymer electrolytes

Firstly, 0.1 wt.% of TiO₂ was added to PEGMEMA solution and dispersed with high-speed stirring at 3,000 rpm to form a homogeneous suspension and LiTFSi was then added to the suspension. Oxygen atom to lithium ion molar ratio was maintained as 20:1. Finally, the initiator BCHPC was added to the mixture solution in a 200:1 PEGMEMA/initiator mass ratio. The solution, prepared as described above, was poured into a Teflon mold and heated at 90 °C for 1 h to obtain a composite solid polymer electrolyte. An illustration of the synthesis of polyacrylate-based solid polymer electrolyte is shown in Scheme 1.

Instrumentation

Ionic conductivities were measured by AC impedance spectroscopy using a Solatron impedance analyzer (SI-1260) and a potentiostat/galvanostat electrochemical interface



Scheme 1 Schematic illustration of the synthesis of polyacrylate-based solid polymer electrolyte

(SI-1286) with a frequency range of 0.1–100 kHz, AC amplitude of 10 mV, and a temperature range of 23–90 °C. The equipment were controlled using Z-Plot electrochemical software purchased from Solatron, Inc. Temperature-dependent conductivities were obtained by placing the electrochemical cell in an oven. At high temperatures/conductivities, the impedance spectra were slanted lines; at low temperatures/conductivities, the impedance spectra consisted of depressed semicircles at higher frequencies and slanted lines at lower frequencies. The resistance was determined from the intercept of the slanted line extrapolated and the real axis of each plot of the impedance spectra [imaginary (Z'') vs. real (Z')]. The specific ionic conductivity, σ , was obtained from $\sigma = l/AR$, where l = distance between the two stainless electrodes, 0.5 cm; for the stainless electrode, A = measured area (1 cm²) and R is the measured resistance (Ω). The compatibility of polymer electrolytes with the stainless electrode was determined by AC impedance analysis under open-circuit conditions at various temperatures. Vogel–Tamman–Fulcher (VTF) equation [20] was used to determine the activation energy, E_a , of the Li ion mobility, with the assumption that the temperature dependence of σ showed VTF behavior:

$$\sigma = AT^{-1/2}e^{-B/(T - T_0)} \tag{1}$$

where A reflects the number of charge carriers, B is the apparent activation energy, and T_0 is the ideal glass transition temperature. The electrochemical stability of the solid polymer electrolytes was determined by cyclic voltammetry (CV). CV was recorded using a potentiostat (Solatron 1287) between 2.8 and 4.3 V at a scan rate of 0.5 mV s⁻¹ using a three-electrode cell. Stainless steel was used as both working electrode and counter-electrode with areas of 1.0 cm² along with a lithium reference electrode. The solid polymer electrolyte filled the space between the working and the counter-electrodes.

X-ray diffraction studies of SPE were carried out using a Shimadzu XD-5 X-ray diffractometer with a (CuK α 1.54178 Å) radiation source. Diffractograms were recorded in the 2θ range from 3–70°, with a step size of 0.02°. Solid-state ⁷Li-NMR spectra were recorded at 116.9 MHz on a Chemagnetics CMX-300 spectrometer. Approximately 10 mg of sample was inserted into a 4.0-mm sample tube. The chemical shifts were externally referenced to lithium ion in 1 mol L⁻¹ LiCl/D₂O solution.

The transference number of the lithium cation, t_{Li+} , was determined using Evans' method [21, 22]. The two lithium electrodes were sandwiched with the SPE for measuring the transference number. The DC voltage ($\Delta V=10$ mV) was applied to these two electrodes until the current reached a steady-state value. AC impedance was measured before and

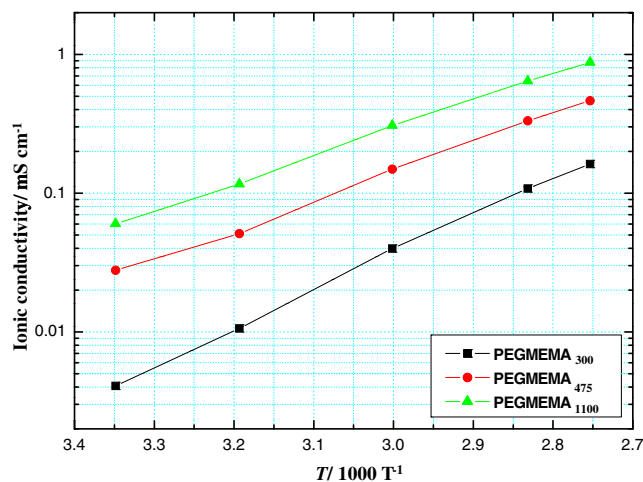


Fig. 1 Temperature-dependent ionic conductivity plots of polyacrylate-based solid polymer electrolytes

after the application of voltage to determine the SPE resistance across the interface. The t_{Li+} value was calculated using the following formula:

$$t_{Li+} = I_{ss} (\Delta V - I_0 R_0) / I_0 (\Delta V - I_{ss} R_{ss}) \tag{2}$$

where ΔV represents the potential applied across the cell and I_0 and I_{ss} are the initial and the steady-state currents, respectively, during the polarization, and R_0 and R_{ss} are the interfacial resistances in the initial and steady states, respectively.

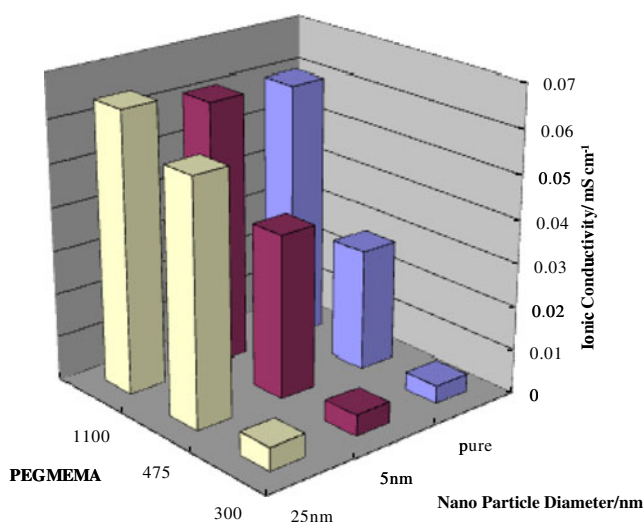


Fig. 2 Ionic conductivity of polyacrylate-based solid polymer electrolytes with various molecular weights (different EO length) and TiO₂ nano-particle diameter at 25 °C

Table 1 Effect of activation energy (E_a / kJ mol⁻¹) of solid-state polymer electrolyte with different-sized nano-composite particles

	Pure electrolyte	Electrolyte + 0.1 wt.% 5 nm TiO ₂	Electrolyte + 0.1 wt.% 25 nm TiO ₂
PEGMEMA ₃₀₀	82.29	16.67	15.37
PEGMEMA ₄₇₅	47.79	14.26	12.31
PEGMEMA _{1,100}	21.62	5.12	3.83

Results and discussion

Ionic conductivity and activation energy analysis of solid polymer electrolytes

The temperature dependence of ionic conductivity for the polyacrylate-based composite polymer electrolytes is shown in Fig. 1. In this figure, a positive relationship between EO side chain length and ionic conductivity of the solid polymer electrolyte was clearly observed. PEGMEMA_{1,100}, with the longest and most flexible EO side chain substituent, achieved a maximum value for ionic conductivity of 6×10^{-5} S cm⁻¹ at room temperature. EO not only provides an active hopping site for lithium cation transfer due to the Lewis acid effect [23], but the EO side chains on PEGMEMA_{1,100} also intertwine with each other, resulting in a significant occupation of the free volume in the polymer electrolyte compared to shorter side chain derivatives [24]. EO side chain length and the free volume dominate the ionic transfer characteristics for the solid polymer electrolyte. In addition, Fig. 1 shows no phase transition when SPE heated to 90 °C, indicating that there was no glass transition point up to this temperature. The ionic conductivity of all the PEGMEMA-based SPEs provided more than 1×10^{-4} S cm⁻¹, and especially PEGMEMA_{1,100} approached 1×10^{-3} S cm⁻¹ at 90 °C.

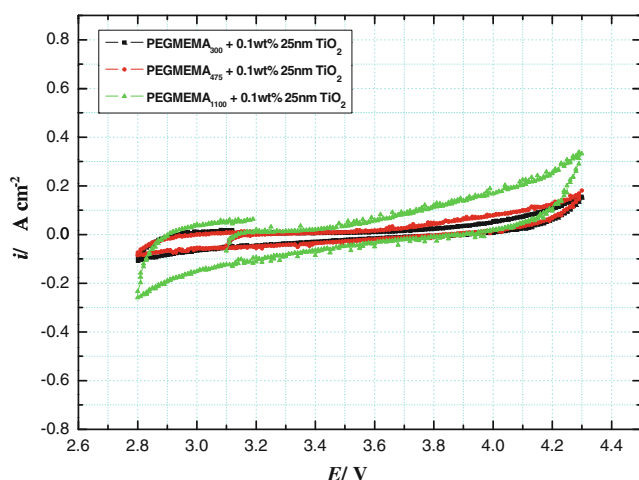
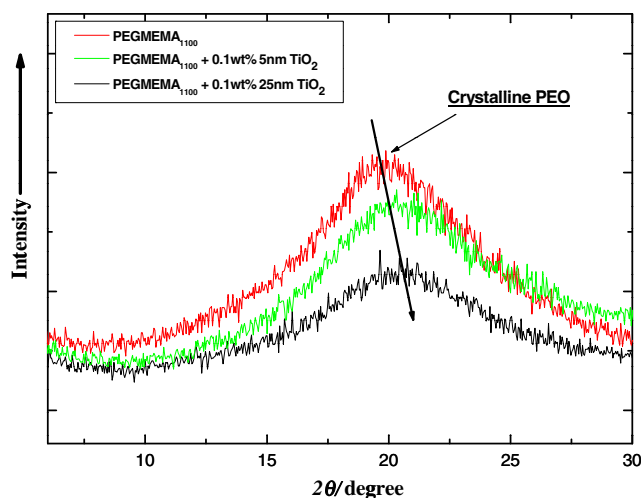
**Fig. 3** Cyclic voltammograms of PEGMEMA and nano-sized TiO₂ composite polymer electrolytes at a scan rate of 0.5 mVs⁻¹

Figure 2 shows the EO side chain length-dependent ionic conductivity of composite PEGMEMA-based SPEs, which were mixed with nano-sized TiO₂ particles of various sizes. In this figure, it is interesting to note that the conductivity increases with increasing SPE EO side chain length. Additionally, improvement in the ionic conductivity of these solid electrolytes is better for larger-sized TiO₂ particles than that of smaller particles. The larger TiO₂ particle effectively increases the separation distance of neighboring EO side chains and improves the overall SPE free volume. Figure 2 also reveals that the ionic conductivity of PEGMEMA₄₇₅ increases more dramatically with the size of the TiO₂ nano-particle than either of the other two PEGMEMA samples. A possible explanation is that PEGMEMA₃₀₀ has lower average molecular weight and shorter EO side chains, suggesting that the polymer structure is rigid and is insensitive to the addition of the ceramic filler. PEGMEMA_{1,100} had the longest side chain and could entangle with other side chains, despite the nano-filler acting to separate the chains apart. However, an increase in the degree of ionic conductivity between 5- and 25-nm-diameter particles was still less than for PEGMEMA₄₇₅, which had both the adequately flexible backbone that polymer electrolytes require and an appropriate length to allow for lithium ion hopping within the SPE ceramic composite.

**Fig. 4** XRD patterns of nano-composite solid-state polymer electrolytes

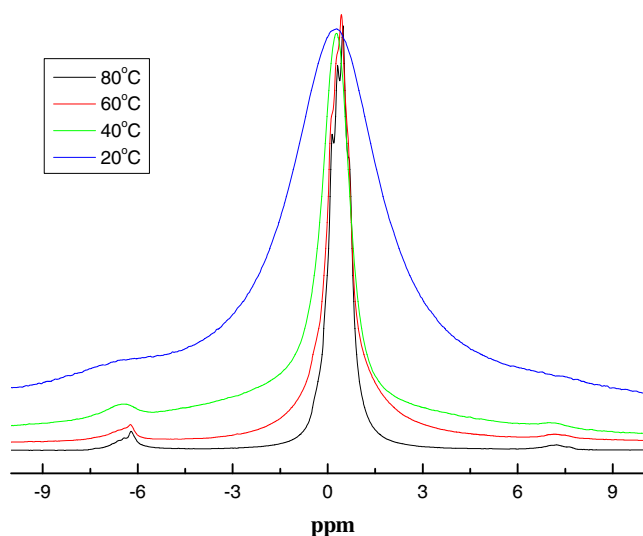


Fig. 5 ^7Li -NMR spectrum of PEGMEMA₃₀₀ nano-composite polymer electrolyte at different temperatures

Table 1 shows that the PEGMEMA-based composite SPE, with ceramic fillers of all tested sizes, produces a large drop in activation energy in comparison to literature values [25]. According to Table 1, the activation energy (E_a) of PEGMEMA₃₀₀ mixed with 0.1 wt.% TiO₂ falls to 16.7 kJ mol⁻¹ and of PEGMEMA_{1,100} to 5.1 kJ mol⁻¹. Above E_a values approach those of gel polymer electrolytes when mixed with a liquid carbonate electrolyte [6, 26]. Thorough mixing of ceramic filler into a precursor solution increases free volume and enhances ionic conductivity, irrespective of the identity of the polymer that is synthesized [27] or of the particular filler that is used [28]. Thus, the use of ceramic additives to improve ionic conductivity is appropriate for industrial applications. In addition, some researches also introduce the nano-sized fillers resulting in the intense interlayering of the polymer membranes with a well-interconnected porous structure [29] and the contribution aims at reconsidering the role of filler in affecting the ionic transport in composite gel electrolyte for Li ion cells based on microporous polymer membranes [30], indicating the free volume for ionic transfer route and dramatically

eliminating the activation energy of polymer electrolyte with filler.

Furthermore, Table 1 shows that the activation energy decreases with increasing particle size and larger ceramic particles show better ionic transfer ability for the same amount of TiO₂ added. The PEGMEMA electrolytes also provide excellent ionic conductivity properties compared to other polymer systems with ceramic filler [31, 32]; therefore, the PEGMEMA electrolytes are possible applications as electrolyte in future polymer batteries.

CV analysis of composite solid polymer electrolyte

Figure 3 shows the cyclic voltammetric results obtained for the three PEGMEMA composite solid polymer electrolyte samples. These data reveal that PEGMEMA-based SPEs are very stable over a battery operation range of 2.8 to 4.3 V and with no apparent side reactions. The cyclic voltammograms (Fig. 3) also show a complete formation of SPE by free radical polymerization and show no surplus precursor side reaction effects regarding further ionic transfer detection. Moreover, the electrochemical behavior of PEGMEMA_{1,100} shows a rather wider current density response range than either of the other two samples. This suggests an enhanced ionic motion and an excellent ionic conductivity of PEGMEMA_{1,100} with nano-ceramic filler.

XRD and NMR analysis of composite solid polymer electrolyte

Figure 4 presents the X-ray diffraction spectra for PEGMEMA_{1,100} SPE with and without 5 and 25 nm TiO₂ fillers. A crystalline PEO peak is seen at 20° and peak intensity weakens with the addition of filler. A more amorphous structure forms with an increase in the particle size of the filler. This observation explains why the filler that dispersed so well into the PEGMEMA_{1,100} sample showed the greatest conductivity and the lowest activation energy. Figure 5 displays the variable temperature ^7Li -NMR spectrum for the PEGMEMA_{1,100} dispersed with 0.1 wt.% 25 nm TiO₂ nano-particles. According to the fundamental NMR theory [33] and previously reported

Table 2 Parameter obtained from the application of a constant potential and impedance to calculate the lithium transference number of solid-state polymer electrolytes. The measurements were carried out at 25 °C

	Pure electrolyte	Electrolyte + 0.1 wt.% 5 nm TiO ₂	Electrolyte + 0.1 wt.% 25 nm TiO ₂
PEGMEMA ₃₀₀	0.41	0.51	0.57
PEGMEMA ₄₇₅	0.52	0.54	0.61
PEGMEMA _{1,100}	0.74	0.61	0.59

result [34], the full width at half-maximum (FWHM) represents an average resolution of the resonating nuclei, which is directly proportional to the characteristics of the detected nuclei, and their chemical environment. Narrowing of the FWHM on heating, as seen in Fig. 5, produces an increase in peak resolution. This result allows the resolution of a single peak at 0.1 ppm, representing the salt of LiTFSi. The FWHM at 20 °C is 932.6 Hz (the NMR machine frequency is 116.9 MHz); the LiTFSi chemical shift remained unchanged as the temperature increased to 80 °C. However, the FWHM reduces with increasing temperature of 40 °C. The FWHM values at 40, 60, and 80 °C are 304.5, 245.1, and 238.1 Hz, respectively. These line-widths also show that T_2 relaxation times are sufficiently long for a non-viscous SPE electrolyte at high temperatures and demonstrate the enhancement to lithium ion motion, which is responsible for the observed improvement in the ionic conductivity. In addition, the two small spinning sideband peaks appeared at -6.1 and 6.4 ppm, revealing the sensitivity of the SPE with an increase in temperature.

Transference number of composite solid polymer electrolyte

Table 2 shows the cation transference number, determined using Evans' DC method [21, 22], for both pure SPE samples and that with the presence of various nano-sized TiO_2 particles. The results show that PEGMEMA_{1,100} without TiO_2 filler shows the highest cation transference value of 0.74, and more generally the transference number decreases with the EO side chain length of PEGMEMA₃₀₀ (0.41) and PEGMEMA₄₇₅ (0.52). The results also verify that the EO side chains are the ionic transfer sites in the SPE. The longer chains also wrap around each other and provide for an ionic transfer hopping pathway. PEGMEMA_{1,100} activation energy is therefore the lowest one of all tested samples. However, the situation changed after the addition of fillers to SPE. The addition of 0.1 wt.% of 5 nm TiO_2 enhances the transference number of PEGMEMA₃₀₀ to 0.51 and of PEGMEMA₄₇₅ to 0.54. Moreover, the addition of larger TiO_2 particles (25 nm) provides a transference number of 0.57 and 0.61 for PEGMEMA₃₀₀ and PEGMEMA₄₇₅, respectively. These results imply that the addition of TiO_2 filler modifies the rigid PEGMEMA₃₀₀ to form a three-dimensional lattice. This process generates extra free volume and so improves the cation transfer performance. An appropriate combination of ceramic filler and molecular chain provided by the addition of large-diameter TiO_2 nano-particles enhances ionic transfer properties such as conductivity and reduces the crystalline characteristics of the polymer. However, the status of PEGMEMA_{1,100} provides longer side chain of EO wrapped around each other and ceramic filler, indicating that the free

volume is being eliminated and hence limits the ionic transfer hopping pathway.

Conclusions

A series of PEGMEMA solid polymer electrolyte samples were prepared by free radical polymerization. The PEGMEMA samples provided excellent room temperature ionic conductivities. In addition, the ionic transfer properties of SPE samples dispersed with nano-filler further enhanced the conductivity. Increasing the size of TiO_2 filler particles removed the crystalline structure of the polymer. The electrochemical properties of SPE, mixed with the TiO_2 filler, revealed that the ionic motion, interaction between EO side chain length and the amount of TiO_2 or the particle size, had a direct influence on the transference number. The addition of larger ceramic nano-particles produces a three-dimensional lattice and increases polymer free volume. Hence, the optimal SPE formulation consists of PEGMEMA_{1,100} with 0.1 wt.% of 25 nm TiO_2 , which is a promising potential candidate for the next generation of polymer battery.

Acknowledgements The authors are grateful for the financial support for this research from the National Science Council of Taiwan, Republic of China, under Grant NSC 99-2218-E-011-008-. The technical assistance from the Materials and Chemical Research Laboratories of the Industrial Technology Research Institute (Taiwan) is appreciated.

References

1. Gray FM (1991) Solid polymer electrolytes, fundamentals and technological applications. VCH, New York
2. Gray FM (1997) Polymer electrolytes. The Royal Society of Chemistry, Cambridge
3. MacCallum JR, Vincent CA (1987 & 1989) Polymer electrolyte reviews 1 and 2. Elsevier, London
4. Wang FM, Hu CC, Lo SC, Wang YY, Wan CC (2009) Solid State Ionics 180:405
5. Wang FM, Hu CC, Lo SC, Wang YY, Wan CC (2010) J Electroanal Chem 644:25
6. Wang FM, Wu HC, Cheng CS, Huang CL, Yang CR (2009) Electrochim Acta 54:3788
7. Joo JH, Bae YC (2008) J Appl Polym Sci 110:2884
8. Wang L, Liang H, Wu J (2010) J Chem Phys 133:44906
9. Zhang Z, Lyons LJ, Amine K, West R (2005) Macromolecules 38:5714
10. Zhang X, Sherlock D, West R, Amine K, Lyons JL (2003) Macromolecules 36:9176
11. Liu Y, Lee JY, Hong L (2004) J Power Sources 129:303
12. Lin CW, Hung CL, Venkateswarlu M, Hwang BJ (2005) J Power Sources 146:397
13. Wang FM, Wan CC, Wang YY (2009) J Appl Electrochem 39:253
14. Park CH, Park M, Yoo SI, Joo SK (2006) J Power Sources 158:1442
15. Ward IM, Hubbard HVStA, Wellings SC, Thompson GP, Kaschmitter J, Wang H (2006) J Power Sources 162:818–822

16. Croce F, Appetecchi GB, Persi L, Scrosati B (1998) *Nature* 394:456
17. Kumar B, Scanlon L, Marsh R, Manson R, Higgins R, Baldwin R (2001) *Electrochim Acta* 46:1515
18. Kumar B, Scanlon LG, Spry RJ (2001) *J Power Sources* 96:337
19. Volel M, Armand M, Gorecki W, Saboungi ML (2005) *Chem Mater* 17:2028
20. Binesh N, Bhat S (1998) *J Polym Sci B* 36:1201
21. Abraham KM, Jiang Z, Corroll B (1997) *Chem Mater* 9:1978
22. Cheng CL, Wan CC, Wang YY, Wu MS (2005) *J Power Sources* 144:238
23. Hwang SS, Cho CG, Kim H (2010) *Electrochem Commun* 12:916
24. Ju H, Sagle AC, Freeman BD, Mardel JI, Hill AJ (2010) *J Membr Sci* 358:131
25. Aravindan V, Vickraman P, Krishnaraj K (2009) *Curr Appl Phys* 9:1474
26. Zhang HP, Zhang P, Li GC, Wu YP, Sun DL (2009) *J Power Sources* 189:594
27. Zhang J, Huang X, Wei H, Fu J, Huang Y, Tang X (2010) *Electrochim Acta* 55:5966
28. Zhang H, Maitra P, Wunder SL (2008) *Solid State Ionics* 178:1975
29. Raghavan P, Zhao X, Manuel J, Chauhan GS, Ahn JH, Ryu HS, Ahn HJ, Kim KW, Nah C (2010) *Electrochim Acta* 55:1347
30. Osińska M, Walkowiak M, Zalewska A, Jesionowski T (2009) *J Membr Sci* 326:582
31. Park JW, Jeong ED, Won MS, Shim YB (2006) *J Power Sources* 160:674
32. Shanmukaraj D, Wang GX, Liu HK, Murugan R (2008) *Polym Bull* 60:351
33. Brighton PWM (2006) *Quart J Roy Met Soc* 104:289
34. Jeon JD, Kwak SY (2006) *Macromolecules* 39:8027