

## Ionic conductivity and dielectric behavior of novel poly(vinyl formal)-based single-ion-conductor polymer electrolytes

Hong-Yan Guan,<sup>1,2</sup> Zhong-Bao Guo,<sup>1</sup> Jian-Jun Ding,<sup>1</sup> Fang Lian<sup>2</sup>

<sup>1</sup>China Building Materials Test and Certification Group, China Building Materials Academy, Beijing 100024, China

<sup>2</sup>School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

Correspondence to: H.-Y. Guan (E-mail: guansuccessful@163.com)

**ABSTRACT:** Novel single-ion-conductor polymer (SCP) electrolytes based on oxalate-chelated-borate-structure-grafted poly(vinyl formal) (PVFM) were synthesized via a solution casting technique. The influence of the molar ratio of —OH and boron atoms in PVFM on the ionic conductivity ( $\sigma$ ) of the SCP electrolytes at different temperatures was investigated with alternating-current impedance spectroscopy in the frequency range of 0.01 Hz to 1 MHz. The results show that  $\sigma$  of the SCP electrolytes at 15–60 °C was about  $10^{-6}$ – $10^{-5}$  S/cm, and temperature dependence of the conductivity of the electrolytes followed the Vogel–Tamman–Fulcher relationship. The dielectric behaviors of the SCP electrolytes were analyzed in view of the dielectric permittivity and dielectric modulus of the electrolytes. Dielectric analysis revealed that the transport of  $\text{Li}^+$  ions in the PVFM-based SCP electrolytes mainly followed a hopping mechanism coupled with the segmental motion of the polymer chain. Additionally, a dielectric relaxation was found in the high-frequency region; this was a thermally activated result and also implied the appearance of carrier hopping. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43510.

**KEYWORDS:** electrochemistry; functionalization of polymers; membranes; properties and characterization

Received 20 October 2015; accepted 3 February 2016

DOI: 10.1002/app.43510

### INTRODUCTION

Solid polymer electrolytes (SPEs) have attracted great interest in past decades because of their intrinsic advances, such as their much better mechanical stability, safety, and flexibility in the design of lithium-ion batteries, and also their wide applications in various electrochemical devices.<sup>1,2</sup> The use of SPEs, in which lithium salt is associated with a polar polymer matrix without organic solvents, could solve most safety issues caused by liquid electrolyte systems.<sup>3</sup> SPEs act as both ionic conductor electrolytes and separators in batteries. Nevertheless, SPEs generally have dual ionic conductivity ( $\sigma$ ), in detail from the anion ( $\text{X}^-$ ) and the lithium cation ( $\text{Li}^+$ ), as a solution of a discrete lithium salt ( $\text{LiX}$ ) in a dissociating medium. A dual-ion conductor is accessible for salt overconcentration or salt depletion; this increases the polarization and also creates strong osmotic forces.<sup>4</sup> Recently, Bouchet *et al.*<sup>3</sup> and Zhu and coworkers<sup>5,6</sup> reported SCPs produced by the grafting of the anions of lithium salts, such as trifluoromethane sulfonimide ( $\text{TFSI}^-$ ), to the polymer main chains, with the simultaneous enhancement of the  $\text{Li}^+$  conductivity and  $\text{Li}^+$  transport number by increasing mobility of the lithium cations. These previous studies have paved the way for a new class of macromolecular electrolytes for lithium-ion batteries.

The study of the dielectric relaxation process in polymeric systems helps us to understand the molecular motions and their interactions, which are immensely affected by the chemical composition, molecular structure, and morphology of the samples.<sup>7</sup> The dielectric parameters associated with the relaxation processes in ion-conduction polymers contribute to the capacity for dissolving salts of a polymer material. For solid or gel polymer electrolytes, the dielectric permittivity generally refers to the relaxation response of an oscillating dipole formed by  $\text{X}^-$  and  $\text{Li}^+$ , where an external electric field is applied as a function of the frequency. Although only  $\text{Li}^+$  cations contribute to the  $\sigma$ s of the electrolytes and  $\text{X}^-$  anions are fixed to the polymer main chain in SCP electrolytes, the behavior of  $\text{Li}^+$  cations and  $\text{X}^-$  anions with the applied external electric field is still unknown to the best of our knowledge. Studying the  $\sigma$  and dielectric behaviors helps us understand the properties of SCP electrolytes.

Recently, we successfully prepared novel poly(vinyl formal) (PVFM)-based dual-ion-conducting polymer electrolytes via an initiator-free thermal polymerization technique<sup>8</sup> and a phase-inversion method,<sup>9</sup> respectively; these showed a high conductivity, wide electrochemical stability, and excellent cycling performance. In our previous work,<sup>10</sup> oxalate-chelated-borate-structure-

grafted PVFM-based SCP membranes were synthesized, and their physical and application properties were carefully characterized. In this study, corresponding gel electrolytes were obtained by the swelling of the plasticizer propylene carbonate (10 wt %); this could improve the positive dielectric permittivity because of the localization of charge carriers.<sup>11</sup> A detailed temperature impedance spectroscopy study of the  $\sigma$  and dielectric behaviors of the SCPs was undertaken to determine the ionic conduction mechanism of the PVFM-based SCP gel electrolytes.

## EXPERIMENTAL

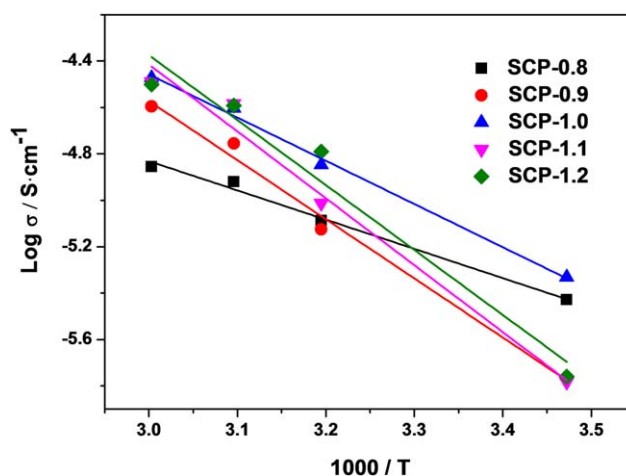
PVFM (Aldrich), with a molecular weight of 70,000, was used as a raw material in which the molar percentages of vinyl acetal, vinyl hydroxyl, and vinyl acetate groups in PVFM were determined to be 62.3, 10.5, and 27.2%, respectively. Boric acid ( $\text{H}_3\text{BO}_3$ ), oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ), lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), and dimethyl sulfoxide (DMSO) were purchased from Sino-pharm Chemical Reagent Co., Ltd.

PVFM and  $\text{H}_3\text{BO}_3$  were dissolved in DMSO with the  $n(-\text{OH})/n\text{B}$  ratios fixed at 2:0.8, 2:0.9, 2:1.0, 2:1.1, and 2:1.2, respectively. Then, the mixtures were magnetically stirred at 80 °C for 4 h to obtain homogeneous and transparent solutions.  $\text{Li}_2\text{CO}_3$  and  $\text{H}_2\text{C}_2\text{O}_4$  powders were added in turn with the molar ratio of  $n(\text{H}_3\text{BO}_3)/n(\text{Li}_2\text{CO}_3)/n(\text{H}_2\text{C}_2\text{O}_4)$  fixed at 2.0:1.0:2.0, and then, the mixed solution was magnetically stirred at 100 °C for 8 h. After being cooled to room temperature, the solution was later cast onto neat glass plates by the doctor-blade method and dried at 70 °C for 12 h to remove the solvent. Finally, the oxalate-chelated-borate-structure-grafted PVFM-based SCP membranes were obtained through the chemical crosslinking reaction among the hydroxyl groups of PVFM,  $\text{H}_3\text{BO}_3$ ,  $\text{Li}_2\text{CO}_3$ , and  $\text{H}_2\text{C}_2\text{O}_4$ . The SCP membrane samples were marked as SCP-0.8, SCP-0.9, SCP-1.0, SCP-1.1, and SCP-1.2, respectively. The membranes were punched into circular pieces, vacuum-dried at 70 °C for 12 h to remove the trace amounts of solvent, and kept in an Ar-filled glovebox for further use.

The SCP gel electrolytes were obtained by the swelling of the plasticizer propylene carbonate (10 wt %); this could improve the positive dielectric permittivity because of the localization of charge carriers. The  $\sigma$ s of the corresponding electrolytes were performed in blocking-type cells fabricated by the sandwiching of the membranes between two stainless steel electrodes and measured by the alternating-current impedance method. Impedance data were obtained with a CHI660a electrochemical working station (Shanghai, China) in the frequency range from 1 Hz to 100 kHz between 25 and 85 °C. The  $\sigma$ s were calculated from eq. (1):

$$\sigma(\text{S/cm}) = L/RS \quad (1)$$

where  $R$  is the bulk resistance,  $L$  is the thickness of the polymer electrolyte, and  $S$  is the area of the stainless steel electrode. The conductivity-temperature studies were carried out in the temperature range between 303 and 373 K. The thickness of the films was measured with a micrometer screw gauge.



**Figure 1.** Conductivities and fitted results for the PVFM-based SCP gel electrolytes prepared with various  $n(-\text{OH})/n\text{B}$  ratios (T: temperature). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The relationships between the complex impedance, dielectric constant ( $\epsilon_r$ ), dielectric loss ( $\epsilon_i$ ), and loss tangent ( $\tan \delta$ ) were calculated by the following equations<sup>12</sup>:

$$Z = Z_r + jZ_i \quad (2)$$

$$\epsilon_r = Z_i / [\omega C(Z_r^2 + Z_i^2)] \quad (3)$$

$$\epsilon_i = Z_r / [\omega C(Z_r^2 + Z_i^2)] \quad (4)$$

$$\tan \delta = \epsilon_i / \epsilon_r \quad (5)$$

where  $Z$  is the impedance of the polymer electrolyte,  $Z_r$  and  $Z_i$  are the magnitudes of the real and imaginary impedance.  $Z_r$  and  $Z_i$  are related to the magnitude of the complex impedance via the equations  $Z_r(\omega) = Z(\omega) \cos \theta(\omega)$ ;  $Z_i(\omega) = Z(\omega) \sin \theta(\omega)$ ;  $C = \epsilon_0 A/t$ , where  $A$  is the effective contact area of the electrode and the electrolyte,  $t$  is the sample thickness,  $\epsilon_0$  is the permittivity of free space; and  $\omega = 2\pi f$ , where  $f$  is the frequency.

## RESULTS AND DISCUSSION

### $\sigma$ Studies

The variation of  $\sigma$  with the reciprocal temperature for the PVFM-based SCP gel electrolytes prepared with different  $n(-\text{OH})/n\text{B}$  ratios is shown in Figure 1. The curvatures of the Arrhenius-type plots indicate that the conductivity-temperature relationship of the SCP gel electrolytes obeyed the Vogel-Tamman-Fulcher relation, which characterizes the transport properties of ions in a viscous matrix.<sup>11</sup> Moreover, the PVFM-based SCP gel electrolytes exhibited conductivities of  $10^{-6}$ – $10^{-5}$  S/cm between 15 and 60 °C. The  $\sigma$  values of the SCP electrolytes were generally lower than that of the dual-ion-conducting system because of the lost conductivity contribution from anion transference. The conductivity of the SCP gel electrolytes increased and then descended with an increase in the crosslinking degree. SCP gel electrolytes showed the highest conductivity of  $3.39 \times 10^{-5}$  S/cm at 60 °C with an  $n(-\text{OH})/n\text{B}$  ratio of 2:1. This was explained by the fact that the increasing number of free  $\text{Li}^+$  ions with increasing crosslinking degree enhanced the conductivity; however, with a further increase in the

**Table I.** Activation Energy for  $\sigma$  of PVFM-Based SCP Gel Electrolytes Prepared with Various  $n(-OH)/nB$  Ratios

Membrane sample	SCP-0.8	SCP-0.9	SCP-1.0	SCP-1.1	SCP-1.2
$n(-OH)/nB$ ratio	2:0.8	2:0.9	2:1.0	2:1.1	2:1.2
Activation energy (kJ/mol)	10.5	21.2	15.5	24.0	23.3

crosslinking degree, the number of free ions almost reached saturation. This led to interference with each other between ions and a reduction of the conductivity.

The Arrhenius activation energy calculated from the linear region in Figure 1 is listed in Table I. The SCP-0.8 and SCP-1.0 based electrolytes exhibited lower activation energies than the other systems, whereas the conductivity of the SCP-1.0 based gel electrolyte was much higher than that of SCP-0.8. The motion of polymer segments resulted in an increase in the free volume of the SCP electrolytes; this, in turn, facilitated the motion of ionic charge and provided a pathway for ionic hopping from one site to another in the SCP electrolytes. At low temperatures, the segmental motion dominated the conduction, whereas at high temperatures, the conduction depended on the amount of charge carrier. Therefore, the polymer chains with a lower activation energy acquired faster bond rotations, which produced strong segmental motions and contributed to the higher conductivity of the polymer electrolyte. Consequently, two competing factors, the segmental mobility, which influenced the mobility of the charge carriers, and the mobile charge carrier concentration, which depended on interaction between the Li ions and the polymer chain,<sup>13,14</sup> were optimized in the electrolyte SCP-1.0, with the highest conductivity.

#### Dielectric Permittivity Studies

The dielectric permittivity represents the stored and loss charges in polymer electrolytes; this is related to dielectric relaxation, that is, the relaxation response of the polymer electrolyte to the applied external electric field as a function of the frequency. Figure 2(a–c) shows the variation of the real part of the dielectric constant ( $\epsilon'$ ), the imaginary part of the dielectric constant ( $\epsilon''$ ), and  $\tan \delta$ , respectively, with the frequency at 60 °C. We observed that the  $\epsilon'$  and  $\epsilon''$  values of all of the electrolytes decreased with increasing frequency and reached saturation in the higher frequency range. The rapid fall of  $\epsilon'$  and  $\epsilon''$  over the frequency range  $10^{-2}$ – $10^2$  Hz was attributed to the tendency for the dipoles in the macromolecules to orient themselves in the direction of the applied field, although the oscillating dipole could not rotate rapidly in the higher frequency range, so the polarization decreased because of the charge accumulation.<sup>15</sup> This resulted in a decrease in the dielectric permittivity.

Both the SCP-0.8 and SCP-1.2 based electrolytes shown in Figure 2(a,b) exhibited the highest  $\epsilon'$  and  $\epsilon''$  values; this implied that the segmental mobility and mobile charge carrier concentration competed for the dielectric behavior of the SCP electrolytes. This suggested that for SCP electrolytes, the flexibility of the polymer main chain dominated the dielectric permittivity at low crosslinking degrees, whereas at higher crosslinking degrees, the crystallinity of the polymer decreased with increasing crosslinking degree. Thus, the  $Li^+$  ion concentration increased and dominated the dielectric permittivity. The  $\tan \delta$  spectra in Fig-

ure 2(c) show the relaxation process for all of electrolytes around  $10^5$  Hz; this was closely related to the electrode polarization. As the crosslinking degree increased, the magnitude of the relaxation peak increased and then decreased with increasing breadth. This indicated that the oxalate-chelated borate structure was attached to the PVFM main chain through the pendent structure groups, which decreased the molecular mobility of the electrolytes.

#### Dielectric Relaxation Studies

$\epsilon'$ ,  $\epsilon''$ , and  $\tan \delta$  for the SCP-1.0 electrolyte as a function of the frequency at different temperatures are shown in Figure 3. The  $\epsilon_r$  ( $\epsilon'$ ),  $\epsilon_i$  ( $\epsilon''$ ), and conductivity exhibited improvements with increasing temperature. It is accepted that the oxygen atoms in the PVFM main chain and also boric atoms in the pendent oxalate-chelated borate structures act as electron acceptors. So, the conduction and dielectric behavior of the SCP electrolytes contributed to the transient dissociation and redissociation between the  $Li^+$  ions and the electron acceptors. In our study, the as-obtained oxalate-chelated-borate-structure-grafted PVFM-based SCP electrolytes showed semicrystalline properties. The partial crystalline phase in the SCPs dissolved gradually into an amorphous phase with increasing temperature,<sup>16</sup> and more ions existed in the polymer electrolytes; this resulted in increases in the free ions and charge carrier density because of the increase in the dissociation and redissociation of  $Li^+$  ion aggregates. Consequently, both the conductivity and  $\epsilon_r$  were enhanced with increasing temperature. Figure 3(c) shows that the relaxation peak of the PVFM-based SCP electrolytes moved to higher frequencies with increasing temperature. The phenomena implied that the enhancing segmental motion of the polymer chain with increasing temperature provided an accessible pathway for  $Li^+$ -ion hopping from one site to another, and this improved the conductivity of the SCPs.

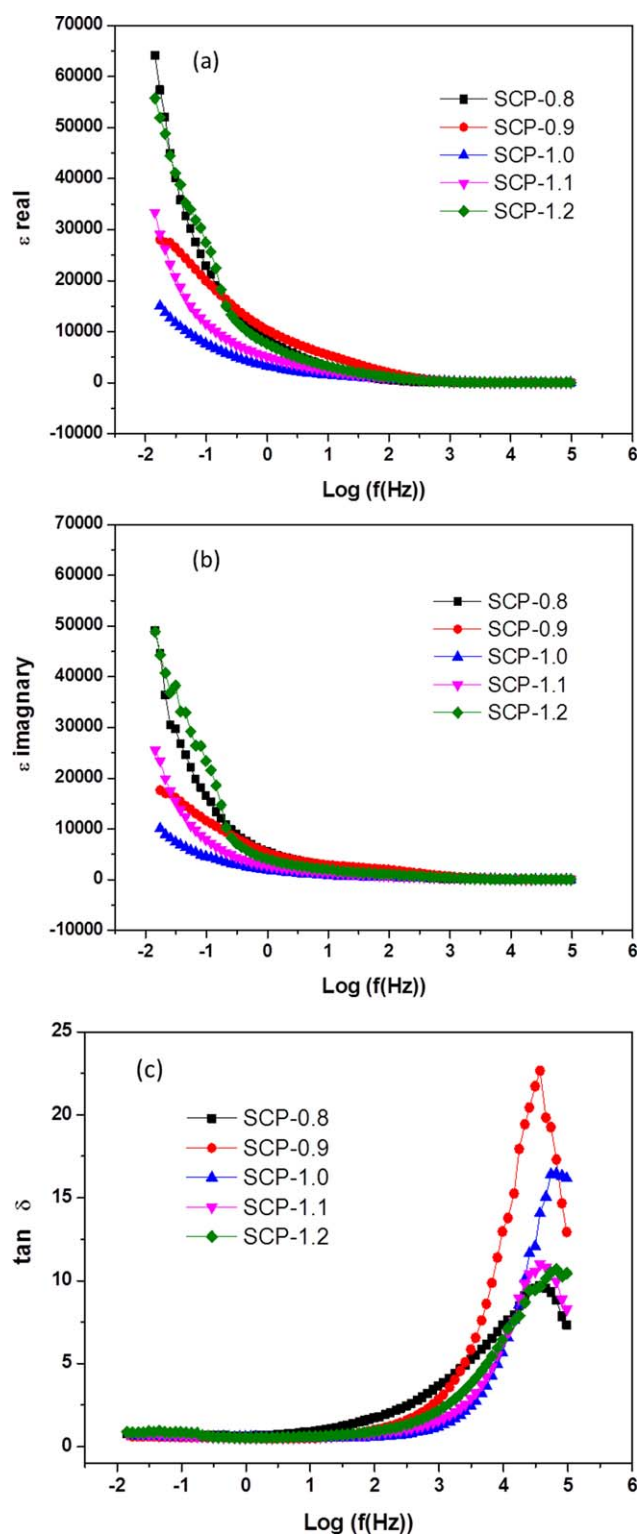
#### Dielectric Modulus Studies

Further analysis of the dielectric behavior of the SCP electrolyte was done with the formulation of dielectric moduli. Figure 4(a,b) shows the real part of the modulus ( $M'$ ) and imaginary part of the modulus ( $M''$ ), respectively, for the SCP-1.0 electrolyte at different temperatures. These plots were obtained by calculation with the following formulas:

$$M' = \epsilon' / [(\epsilon')^2 + (\epsilon'')^2] \quad (6)$$

$$M'' = \epsilon'' / [(\epsilon')^2 + (\epsilon'')^2] \quad (7)$$

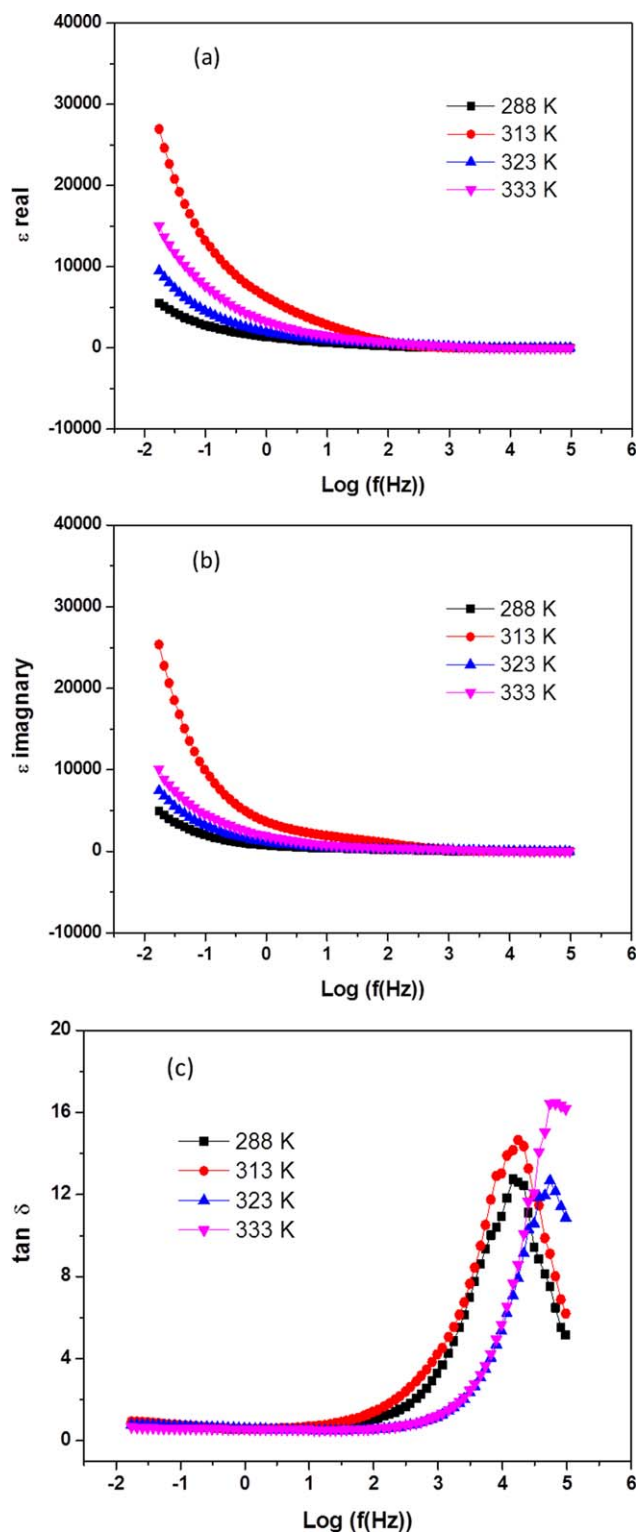
Both  $M'$  and  $M''$  exhibited a single relaxation peak. The  $M'$  and  $M''$  values approached zero quickly in the lower frequency range; this implied that the electrode polarization effect made a negligible contribution to the modulus. No characteristic peak was observed at 288 K for the SCP-1.0 electrolyte. The peak of the electrolyte appeared around 100 Hz at 313 K and slowly shifted to a higher frequency as the temperature increased. This implied that the SCP electrolyte was a definite ionic conductor,



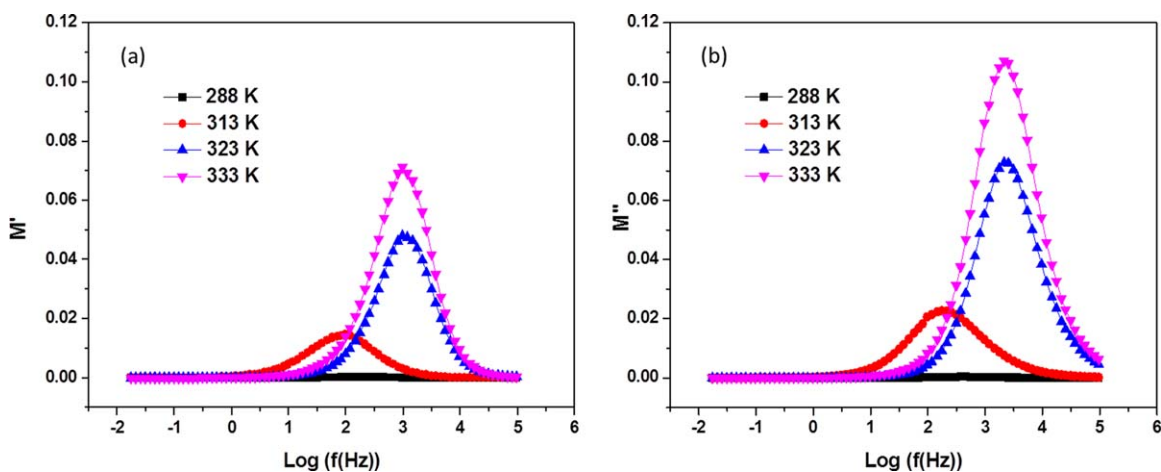
**Figure 2.** Variation of (a)  $\epsilon'$ , (b)  $\epsilon''$ , and (c)  $\tan \delta$  for PVFM-based SCPs as a function of the frequency at 60 °C ( $\epsilon$ : dielectric constant). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and its properties were correlated with the conductivity process. According to a report on polymer electrolytes by Karmakar and Ghosh,<sup>17</sup> the region to the left side of the peak is where the

positive ions are mobile over long distances, whereas the region to the right is where the ions are spatially confined to their potential wells. Additionally, Figure 4(a,b) also shows that both



**Figure 3.** Variation of (a)  $\epsilon'$ , (b)  $\epsilon''$ , and (c)  $\tan \delta$  with the frequency for SCP-1.0 at different temperatures ( $\epsilon$ : dielectric constant). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** Variation of (a)  $M'$  and (b)  $M''$  spectra with the frequency at various temperatures for SCP-1.0. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$M'$  and  $M''$  increased with temperature; this was attributed to the faster mobility of  $\text{Li}^+$  ions and decreased relaxation time of SCP-1.0 with increasing temperature. The results indicate that the relaxation was thermally activated and charge carrier hopping occurred at a certain temperature; this was in agreement with the report by Furlani *et al.*<sup>18</sup> in which the ions appeared to be bound as ion-pair dipoles on short timescales, whereas at least one in each pair was free to move during longer timescales and gave rise to  $\sigma$ .

## CONCLUSIONS

A series of oxalate-chelated-borate-grafted PVFM-based SCP electrolytes with  $n(\text{—OH})/n\text{B}$  ratios ranging from 2:0.8 to 2:1.2 were synthesized through the crosslinking reaction of PVFM,  $\text{H}_3\text{BO}_3$ ,  $\text{Li}_2\text{CO}_3$ , and  $\text{H}_2\text{C}_2\text{O}_4$  in the presence of DMSO. The temperature dependence of  $\sigma$  of the SCP electrolytes obeyed the Arrhenius relationship, and SCP had a conductivity of  $10^{-6}$ – $10^{-5}$  S/cm at 15–60 °C. Two competing factors, the segmental mobility of the polymer chain and the charge carrier concentration, were optimized in the SCP-1.0 electrolyte with a highest conductivity. The low-frequency dispersion of  $\epsilon_r$  and  $\epsilon_i$  arose from the electrode polarization effect; this confirmed that the SCP gel electrolytes were ionic conductors. The transport of  $\text{Li}^+$  ions in the PVFM-based SCP electrolytes mainly followed the hopping mechanism coupled with the segmental motion of the polymer chain. The conductivity and  $\epsilon_r$  studies indicated that the novel oxalate-chelated-borate-grafted PVFM-based SCP electrolytes possess promising characteristics as electrolytes for lithium-ion batteries, even with only a macropolymer host and  $\text{X}^-$  anions and  $\text{Li}^+$  cations as mobile ions. The properties need further improvement via modification by additives, such as ionic liquids.

## ACKNOWLEDGMENTS

This work was financially supported by the National High-Tech Research and Development Program (contract grant number 2013AA050901).

## REFERENCES

- Ramesh, S.; Lu, S. C.; Morris, E. J. *Taiwan Inst. Chem. E* **2012**, *43*, 806.
- He, D.; Kim, D. W.; Park, J. S.; Cho, S. Y.; Kang, Y. K. *J. Power Sources* **2013**, *244*, 170.
- Bouchet, R.; Maria, S.; Meziane, R.; Aboulaich, A.; Lienafa, L.; Bonnet, J. P.; Phan, T. N. T.; Giames, D.; Devaux, D.; Denoyel, R.; Armand, M. *Nat. Mater.* **2013**, *12*, 452.
- Meziane, R.; Bonnet, J. P.; Courty, M.; Djellab, K.; Armand, M. *Electrochim. Acta* **2011**, *57*, 14.
- Zhu, Y. S.; Wang, X. J.; Hou, Y. Y.; Gao, X. W.; Liu, L. L.; Wu, Y. P.; Shimizu, M. *Electrochim. Acta* **2013**, *87*, 113.
- Zhu, Y. S.; Gao, X. W.; Wang, X. J.; Hou, Y. Y.; Liu, L. L.; Wu, Y. P. *Electrochem. Commun.* **2012**, *22*, 29.
- Rellick, G. S.; Runt, J. *J. Polym. Sci.* **1986**, *24*, 279.
- Guan, H. Y.; Lian, F.; Xi, K.; Ren, Y.; Sun, J. L.; Kumar, R. V. *J. Power Sources* **2014**, *245*, 95.
- Ren, Y.; Lian, F.; Wen, Y.; Guan, H. Y. *Polymer* **2013**, *18*, 4807.
- Lian, F.; Guan, H. Y.; Wen, Y.; Pan, X. R. *J. Membr. Sci.* **2014**, *469*, 67.
- Baskaran, R.; Selvasekarapandian, S.; Hirankumar, G.; Bhuvaneshwari, M. S. *J. Power Sources* **2004**, *134*, 235.
- Othman, L.; Chew, K. W.; Osman, Z. *Ionics* **2007**, *13*, 337.
- Uma, T.; Mahalingam, T.; Stimming, U. *Mater. Chem. Phys.* **2005**, *90*, 239.
- Ramesh, S.; Chai, M. F. *Mater. Sci. Eng. B* **2007**, *139*, 240.
- Ramesh, S.; Wong, K. C. *Ionics* **2009**, *15*, 249.
- Awadhia, A.; Patel, S. K.; Agrawal, S. L. *Prog. Cryst. Growth Charact. Mater.* **2006**, *52*, 61.
- Karmakar, A.; Ghosh, A. *Curr. Appl. Phys.* **2012**, *12*, 539.
- Furlani, M.; Stappen, C.; Mellander, B. E.; Niklasson, G. A. *J. Non-Cryst. Solids* **2010**, *356*, 710.