Conductive performances of solid polymer electrolyte films based on PVB/LiClO$_4$ plasticized by PEG$_{200}$, PEG$_{400}$ and PEG$_{600}$

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ABSTRACT

Solid polymer electrolyte (SPE) films consisting of polyvinyl butyral (PVB) as host polymer, LiClO$_4$ as alkali salt at mole ratio of [O]:[Li] = 8, and different molecular weight polyethylene glycol (PEG) including PEG$_{200}$, PEG$_{400}$, and PEG$_{600}$ as plasticizers are prepared by physical blending method. The dielectric relaxation and electrochemical impedance measurements reveal that the conductive performances are improved by adding PEG as plasticizers through the enhancement in the moving space for ions, and PEG$_{400}$ performs plasticizing effect superior to PEG$_{200}$ and PEG$_{600}$. Their conductivity is measured by using a sandwiched Pt/SPE/Pt cell model. SPE with 30% PEG$_{400}$ (wt%) of PVB exhibits the maximum conductivity at room temperature, and its conductivity increases linearly with temperatures from 303 to 333 K at two to three orders of magnitude higher than that of the other two SPEs containing 30% PEG$_{200}$ and 30% PEG$_{600}$, respectively. However, their conductivity does not increase linearly with the increase in heating temperatures until the temperature reaches around 333 K; the decrease in conductivity with heating from their maxima is attributed to the restriction of ion moving space because of the crosslinking reaction between hydroxyl and aldehyde groups. As observed from the XRD and the microscopy results, PEG$_{400}$ is more effective than others in enhancing the conductive performances of these SPEs through changing LiClO$_4$ from crystalline to amorphous state, increasing the flexibility of PVB, disturbing the short distance sequential order of PVB chains, and promoting the formation of 'pathway' for ions' movement.

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1. Introduction

Solid polymer electrolyte (SPE) has attracted considerable attention in terms of its scientific importance and applications in energy storage or conversion devices such as batteries, fuel cells, super capacitors, etc., arising from its steady ionic conductivity, electrochemical, interfacial stability and good mechanical properties [1–3]. Besides the most frequently used poly(ethylene oxide) (PEO) [4–6], a few classes of polymers such as poly(methyl methacrylate) (PMMA) [7], PVdF [8], PVA [9], etc., were also used as polymer matrixes to develop various solid polymer electrolytes (SPEs). However, almost all of these SPEs showed low ion conductivity and high interfacial resistance due to their chemical or/and physical characteristics which restricted the mobility of ions.

In order to overcome these drawbacks, adding plasticizers in SPEs was considered one of the most effective ways to bring a desirable enhancement in their conductivity by improving the mobility of ionic or/and the interfacial interaction among ionic and polar groups in polymer chains [1,4–7]. Pradhan et al. [1] reported that composite polymer electrolyte based on poly(ethylene oxide)–NaClO$_4$ dispersed with a ceramic filler (SnO$_2$) had a substantial enhancement in the electrical conductivity by two orders of magnitude at room temperature if it was plasticized with polyethylene glycol (PEG$_{200}$). Ali et al. [7] demonstrated that the conductivity of PMMA-based gel electrolytes by using LiN (CF$_3$SO$_2$)$_2$ or LiCF$_3$SO$_3$ as the salt could be improved from 10^{-8} to the range of 10^{-6} to 10^{-4} S cm^{-1} by using propylene carbonate (PC) and ethylene carbonate (EC) plasticizers. In a recent study, Choi et al. [8] found that organic additives could reduce the interfacial resistance in the porous poly(vinylidene fluoride-*co*-hexafluoro-propylene) membrane cell during cycling, and it thus exhibited less capacity fade and better high rate performance. Lee et al. [10] prepared SPEs based on polyethylene non-woven matrix with good mechanical strength and its conductivity could even reach 3.1×10^{-4} S cm^{-1} at room temperature by adding PEG as plasticizers. So far, various organic compounds or low molecular weight polymers such as PC, EC, PEG, etc., were reported having effective plasticizing functions, however, in view of safety in applications, low molecular weight polymers with their nonvolatile nature at heating would be much more valuable. Among these polymers, PEG with various molecular weights were used to make SPEs with some desired conductive performances in the literature [1,4,10], however

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the difference of PEG with different number of repeating units in plasticizing SPEs has not been reported yet.

The conductive performances of SPEs also strongly depended on the types and concentrations of ionic used, and usually fluctuated with the environmental temperatures [6–13]. Ali et al. [7] also demonstrated that in plasticized PMMA-LiX [X: $CF_3SO_3^-$, $N(CF_3SO_2)_2^-$] polymer electrolytes, the conductivity was strongly dependent on salt concentrations and a maximum conductivity for LiTFSI and LiTF respectively at 35 wt% LiX could be reached. Anantha and Hariharan [11] found that solid polymer electrolyte films based on poly(ethylene oxide) (PEO) and $NaNO_3$ salt with compositions between 2 and 10 ether oxygen per sodium could achieve maximum ionic conductivity of $\sim 3.5 \times 10^{-6}\,S\,cm^{-1}$ at room temperature for the composition O/Na = 3:1. In their earlier report, Ali et al. [13] proposed that the increase in conductivity upon addition of salt was attributed to the increase in the number of free ions and the expansion in amorphous region, while the decrease in conductivity up excess addition of salt was attributed to the formation of neutral ion pairs or reduction of vacant coordinating sites. Apart from the composition, temperature also has great effect on the conductivity of SPEs, and the temperature dependence of conductivity was reported mostly in the form of Arrhenius plot which could be well fitted by the Vogel–Tamman–Fulcher (VTF) function in certain temperature ranges; nevertheless, there were also some exceptions reported in the literature where conclusive explanations were not achieved [4,12,14,15].

Since various factors had complex effects on the conductive performances of SPEs associate with their stability and the ion transporting mechanism, some scientific and technological issues need to be solved prior to their wide applications. In this study, SPEs based on polyvinyl butyral (PVB) as host polymer by proportional addition of $LiClO_4$ as salt, and PEG with different molecular weight as plasticizers were prepared. Their conductive performances were evaluated by dielectric constant and AC impedance measurements, while their structure and morphology were detected by X-ray diffraction (XRD) and Digital Microscopy measurements.

2. Experimental

2.1. Reagents

Polyvinyl butyral (PVB) (Mn = 98,400, number of structure butyl units n = 300, CR), used as received; Lithium perchlorate trihydrate ($LiClO_4 \cdot 3H_2O$, AR), dried under vacuum before use; Polyethylene glycol(PEG_{200}, PEG_{400} and PEG_{600}, AR), used as received. These chemicals were purchased from Beijing Chemical Reagent Company. Ethanol (99.7%, AR), used as received, and was purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of polymer electrolyte film

$LiClO_4$ was put in a beaker with ethanol under magnetic stirring to obtain a clear solution, and then certain amount of PVB was added under continuously stirring for about 1 h to get transparent viscous solution (the masses of PVB was calculated based on mole ratio of [O]:[Li$^+$], where [O] represents the mole number of oxygen atom in butyl units, [Li$^+$] represents the mole number of Li$^+$ in $LiClO_4$ salt). Several samples with [O]:[Li$^+$] = 2:1, 4:1, 6:1, 8:1 10:1 and 12:1, respectively were prepared. Afterwards, different amount of PEG_{200}, PEG_{400} or PEG_{600} as plasticizers was added to the mixtures to gain an achromatic and viscous electrolyte solution. To make the free standing films, the above slurry polymer electrolytes were spread onto a mould and left for slow evaporation at room temperature. Then the films were dried in a vacuum oven at 40 °C for 48 h. The final composite polymer films were in a thickness about 0.3–0.7 mm.

2.3. Instruments and measurements

The dielectric constant of the solid electrolyte films were measured by using an impedance analyzer Agilent 4294A in the frequency ranges of 100–10^6 MHz. Before the measurement, the solid electrolyte films were deposited with Ag on the both sides of all samples. Electrochemical impedance spectroscopes of films were measured by using the CHI 660C electrochemical station (Zhenhua Instrument Corp., China) in a three-electrode electrochemical cell with an exposed area 1 cm^2. A platinum sheet and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The electrochemical behavior of films were evaluated during exposure to 3.5 wt% NaCl solution (open to air) over a frequency range of 1–10^5 Hz and the scan rate applied was 5 mV s^{-1}. The electrical conductivity of the composite polymer electrolyte films was measured by using the above electrochemical station equipped with ZSimpWin software with a film sandwiched between symmetric platinum (Pt) electrodes (Pt/polymer electrolyte film/Pt model) [12,16]. The measurements were carried out over a frequency range of 1–10^5 Hz at room temperature. The sample for the ionic conductivity measurement had a square shape with 1 cm in length and 0.3–0.7 mm in thickness. In order to measure the conductivity with temperatures, the Pt/polymer electrolyte/Pt testing cell was put in a heating chamber at heating rate of 2 °C min^{-1} in which the testing temperature could be precisely controlled from room temperature to 200 °C with fluctuation ± 1 °C; The measurement began after it reached the testing temperature and had stayed for 1 min. The ionic conductivity (σ) of the PVB gel electrolyte films can be calculated by the equation: $\sigma = d/(R_b \cdot S)$. Herein σ is the conductivity, R_b is the bulk resistance obtained from the software, d is the distance of the two platinum electrodes, i.e., the thickness of the films, and S is the interface area between platinum electrode and PVB electrolyte with contact area S = 1 cm^2. The X-ray diffraction (XRD) patterns of the samples were recorded by using a PW3710 (Philips) X-ray diffractometer with Cu Kα radiation in the 2θ range from 2.5° to 45° at a scan speed of 2° min^{-1}. The surface morphological features of different composite electrolyte films were observed by using VHX-100K Digital Microscope (KEYENCE Corporation, Japan).

3. Results and discussion

3.1. Dielectric properties

As a way of studying the ionic transport mechanism of SPE, dielectric constant measurement plays an important role in evaluating the dielectric relaxation behavior associate with their ionic conductive characteristics upon frequency [14,17]. Fig. 1 shows the dielectric constant ε as a function of frequency for (a) PVB/$LiClO_4$ SPE films with PEG_{200}, PEG_{400} and PEG_{600} as plasticizers, and (b) PVB/$LiClO_4$ SPE films with PEG_{400} at different amount, respectively. In the entire frequency region tested, the higher values of ε for the plasticized system are due to the enhanced charge carrier density in the space charge accumulation region [11]. However, in the ranges of frequency lower than 10^5 Hz, the ε value of the plasticized samples shows a dramatic loss, till it reaches a trend of nearly stable value with small dispersions with the increase in frequency. Similar onsets of dielectric relaxation transition with frequency were also observed in other SPEs [11,14] and the mechanism was depicted in terms of ion mobility, charge space, dipole relaxation of the polymer segments and the interface interaction between electrode and electrolyte. The low-frequency depression region here is attributed to the contribution of charge accumulation at the electrode/electrolyte interface, where the diffusion and transportation of Li$^+$ are improved with the increase in frequency. The high-frequency saturation range indicates the effective
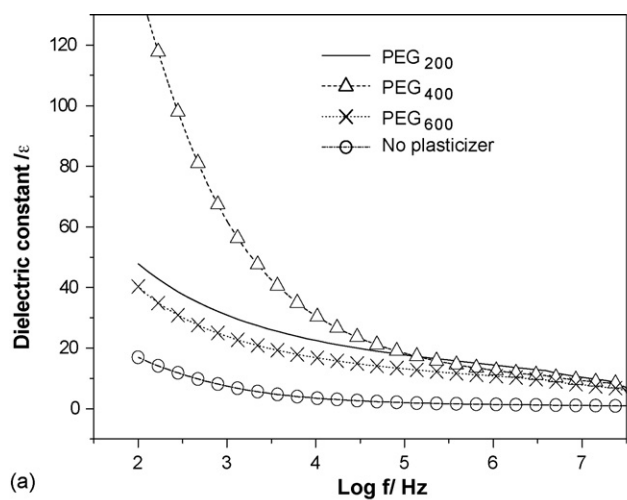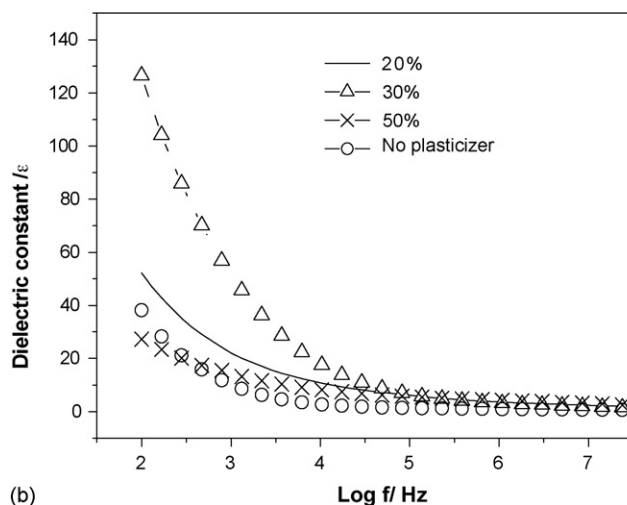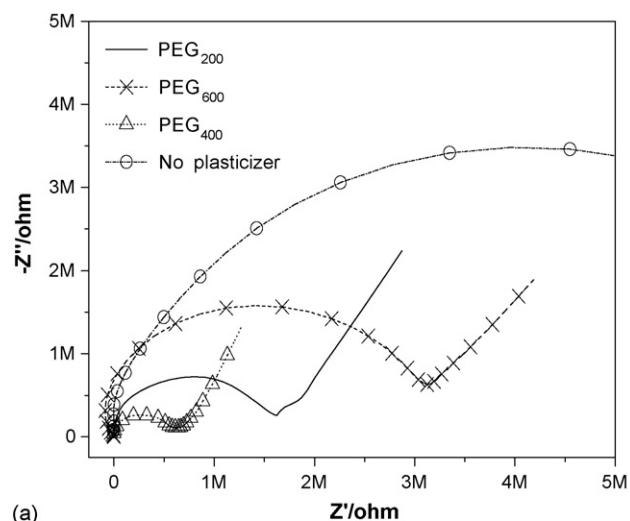
Fig. 1. Dielectric constant ε of solid electrolyte films as a function of frequency for (a) PVB/LiClO$_4$ with plasticizers and (b) PVB/LiClO$_4$ with PEG$_{400}$ at different contents.

Fig. 2. Ac impedance spectroscopy of solid electrolyte films for (a) PVB/LiClO$_4$ with plasticizers and (b) PVB/LiClO$_4$ with PEG$_{400}$ at different contents in 3.5 wt% NaCl solution.
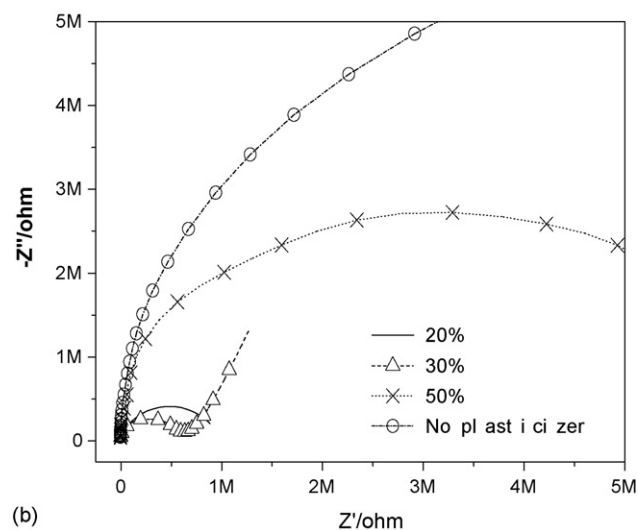
involvement of dipoles of PVB associated with PEG in dielectric polarizations and the enhancement in Li$^+$ mobility [14]. Furthermore, as presented in Fig. 1a, the ε value of PEG does not exhibit regular changes with its molecular weight as a variation; PEG$_{400}$ shows plasticizing effect superior to the other two. More importantly, as shown in Fig. 1b, the ε value is strongly dependent on the amount of PEG$_{400}$ added; excess addition of PEG$_{400}$ results in an obvious reduction in its plasticizing function to SPEs. By comparison, polymer electrolyte containing 30 wt% PEG$_{400}$ exhibited conductive performances superior to other compositions.

3.2. Electronic impedance of SPE thin-film in NaCl solution

Fig. 2 shows the electronic impedance spectroscopy (EIS) (Nyquist plots) of electrolyte films exposed to 3.5 wt% NaCl solution for (a) PVB/LiClO$_4$ SPE films with PEG$_{200}$, PEG$_{400}$ and PEG$_{600}$ as plasticizers, and (b) PVB/LiClO$_4$ SPE films with PEG$_{400}$ at different amount, respectively. The diagrams are composed of partially overlapped semicircle and a straight slopping line at low-frequency end. In these plots, the size of the semicircle reflects the sum of solution resistance Rs and charge transfer resistance Rct; since the measurements were tested in the same solution, Rs is the same, this means that the size of the semicircle can account for the difference of Rct [18]. Since Rct represents the charge transfer process between the interface of film electrode and electrolyte

solution, the ionic conductive behavior of the electrolyte films in NaCl solution could be compared [19]. The smaller Rct suggests the easier Li$^+$ mobility because of the increase in moving space of the ionic in the film, in turn the increase in conductivity of SPEs. As shown in Fig. 2a and b, the Rct of SPE films increases in the order of no plasticizer > PEG$_{600}$ > PEG$_{200}$ > PEG$_{400}$, while the Rct of SPE films containing PEG$_{400}$ increases in the order of 50% > 20% > 30% of PVB; that is, if the addition of PEG$_{400}$ reached 30% of PVB, the Rct attained minimum, indicating that a maximum conductivity could be achieved by adding PEG$_{400}$ at 30% of PVB.

3.3. Ionic conductivity of SPE thin-film in contact with metal electrodes

The conductive behavior of SPEs in contact with solid electrode could be also evaluated by using EIS analysis by using 'Metal electrode/SPEs/Metal electrode cell' model [4,12]. Fig. 3 shows the EIS results of these PVB/LiClO$_4$/plasticizer solid electrolyte films tested by this model. The Nyquist plots are composed of partially overlapped semicircle and a straight slopping line at low-frequency end, where the line with circle (o) represents the tested data, while the line with star (*) represents the simulating line with the equivalent circuit by ZSimpWin software as shown in Fig. 4. The curves
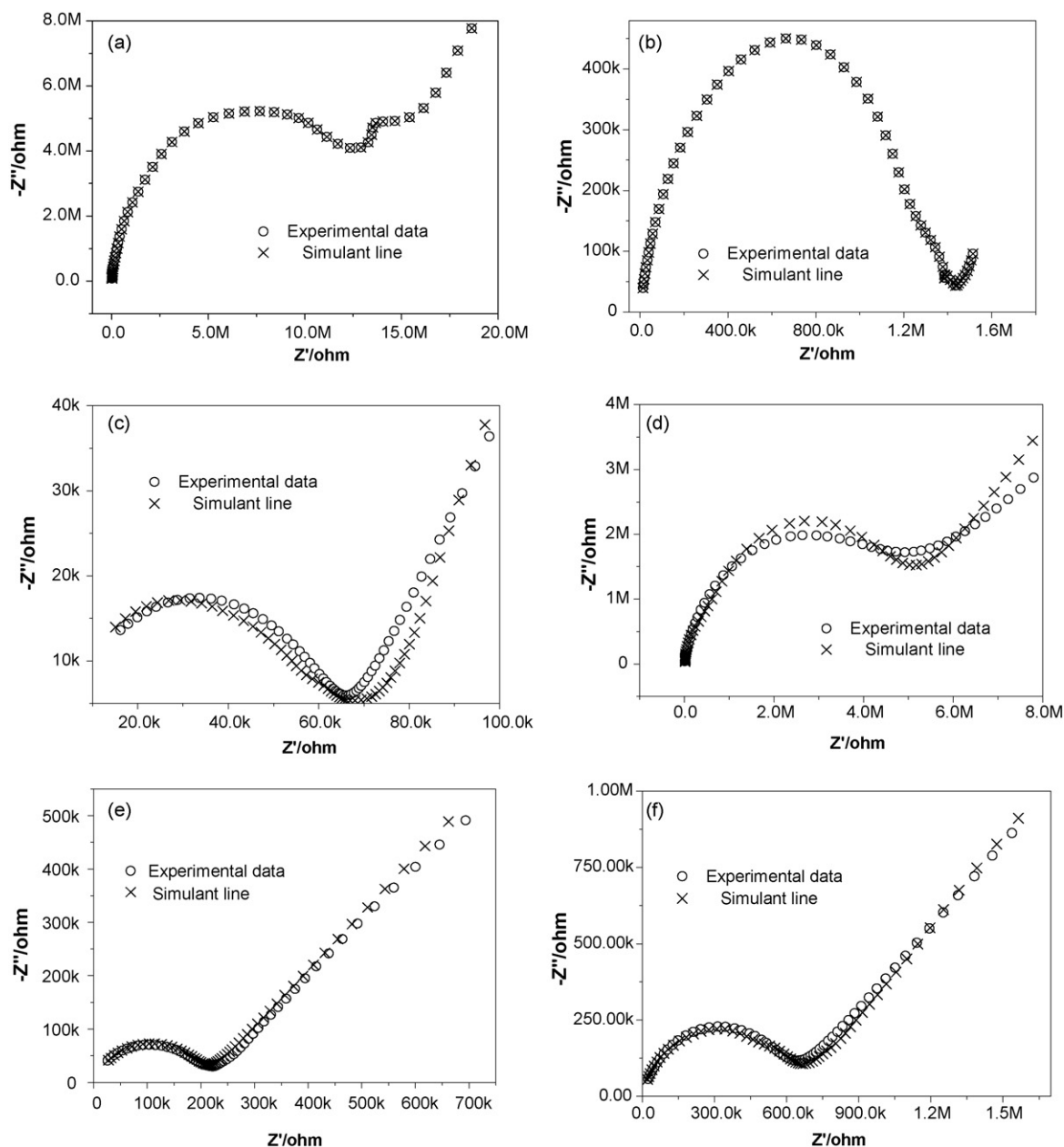
Fig. 3. Diagrams of simulating and experimental impedances of polymer electrolytes measured as 'Pt/electrolyte films/Pt cell' for (a) $PVB/LiClO_4$, (b) $PVB/LiClO_4/30\%$ PEG_{200}, (c) $PVB/LiClO_4/30\%$ PEG_{400}; (d) $PVB/LiClO_4/30\%$ PEG_{600}; (e) $PVB/LiClO_4/20\%$ PEG_{400}; (f) $PVB/LiClO_4/50\%$ PEG_{400}. "%" is the wt% of PVB.

of simulant lines and experimental data matched well in the testing range, indicating the rationality of the equivalent circuit. In Fig. 4, R_b is the bulk resistance of the cell, which reflects a combined resistance of the electrolyte, separator and electrodes; CPE_3 and Cg correspond to the semicircle at high frequencies; CPE is the constant phase element, CPE_1 and CPE_2 correspond to the straight sloping line at low-frequency end representing the relative double-layer capacitances of the interfaces between Pt electrodes and SPEs films.

R_b was gained from the simulating data provided by ZSimpWin software. Based on the corresponding thickness of the electrolyte film, the ionic conductivity was calculated by using the equation $\sigma = d/(R_b \cdot S)$ and the results are shown in Table 1. It is clear that the addition of ions in plasticizer has a remarkable effect on the transportation of the electrolyte. The conductivity value of the $PVB/LiClO_4$ was found to increase from 10^{-10} to 10^{-6} with the addition of 30% PEG_{400} of PVB. The increase in conductivity with the

addition of plasticizers may be due to increase in flexibility of PVB, the increase in fraction of the amorphous phases and the improvement in ion dissociation effects for ionic conduction; among them, PEG_{400} is more effective in these plasticizing functions [14,16].

In Table 2, the double-layer capacitances CPE_1 and CPE_2 exhibit different values, and the CPE_1 values are always larger than CPE_2

Table 1
Calculation of conductivity (σ) of $PVB/LiClO_4$/plasticizers.

Samples	R_b (Ω)	d (cm)	σ ($S\,cm^{-1}$)
No plasticizer	6.33×10^7	0.0367	5.80×10^{-10}
PEG_{200}(30%)	6.98×10^5	0.0324	4.64×10^{-8}
PEG_{400}(30%)	3.24×10^4	0.0698	2.15×10^{-6}
PEG_{600}(30%)	4.05×10^6	0.0169	4.18×10^{-9}
PEG_{400}(20%)	1.90×10^5	0.0383	2.01×10^{-7}
PEG_{400}(50%)	2.93×10^5	0.0226	7.72×10^{-8}

R_b based on the equivalent circuit (Fig. 3) by ZSimpWin software.
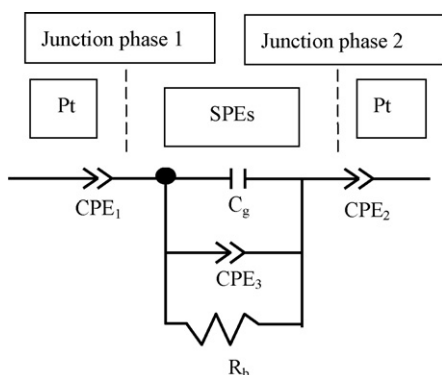
Fig. 4. Equivalent circuit for Pt/solid polymer electrolytes/Pt cell.

Table 2
Relative double-layer capacitances of PVB/LiClO$_4$/PEGs electrolyte films.

Samples	CPE$_1$ (F)	CPE$_2$ (F)
No plasticizer	2.82×10^{-8}	1.11×10^{-9}
PEG$_{200}$(30%)	2.46×10^{-8}	7.25×10^{-9}
PEG$_{400}$(30%)	5.03×10^{-5}	3.38×10^{-8}
PEG$_{600}$(30%)	8.39×10^{-6}	3.20×10^{-9}
PEG$_{400}$(20%)	4.50×10^{-8}	7.76×10^{-9}
PEG$_{400}$(50%)	2.90×10^{-7}	6.05×10^{-9}

Data obtained from the equivalent circuit in Fig. 3 by ZSimpWin software.

values for all the samples, indicating that the charge transportations between the interfaces from Pt to SPEs (depicted as 'junction phase 1' in Fig. 4) and the interfaces from SPEs to Pt (depicted as 'junction phase 2') are different. It seems that the conductive performances among the solid interfaces exhibit orientation towards the electric field applied. Compared to Pt, the conductivity of SPEs is low; it could be inferred that the voltage reduction along the SPEs made it more difficult for charge transporting from SPEs to Pt in the interfaces of 'junction phase 2'. However, the existence of interface charge transporting difference between metal electrodes and SPE need to be proved by other proofs and the mechanism also need to be further elaborated.

3.4. Temperature dependence of conductivity

Fig. 5 shows the temperature dependence of conductivity of SPEs based on PVB with different molecular weight PEG as plasticizers in the temperature range from 303 to 353 K. All the samples exhibit linear increases in conductivity with temperatures till maxima at around 333 K (60 °C), which can be described by Arrhenius relationships as mostly reported in the literatures where the plas-
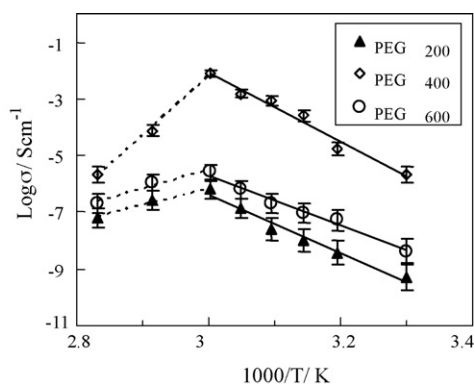
ticizers were considered to change some crystalline regions of polymer matrix to amorphous state so that the ion mobility could be improved [1–8]. However, polymer chains of PVB in this study possessed high amorphous domains (please refer to 3.6 XRD study) rather than high crystalline state like PEO, the function of plasticizers can not be considered as promoters in transferring polymer chain stacks from crystalline to amorphous. With the increase in temperature, the mobility of PVB chains is improved, PEG as a plasticizer promotes the mobility of both PVB chains and ions so that the conductivity of SPE can be improved. However, in this temperature range, SPE containing 30% PEG$_{400}$ exhibits conductivity at two to three order magnitude higher than that of the other two samples, indicating that PEG$_{400}$ provides even much more effective help in enlarging the moving spaces for ions [14,16]. Furthermore, the greater deviation of conductive data from the trend line for SPE containing 30% PEG$_{400}$ provides another fact that its conductivity may be affected by more factors. At an appropriate composition, PEG$_{400}$ may be more effective in promoting the 'pathway' formation so that free volumes for ions movement can be improved further, while the mobility in the 'pathway' is much more sensitive to temperatures.

The obvious depression in conductivity upon heating temperatures above 60 °C are attributed to the network formation among PVB and PEG chains since the hydroxyl group can react with the aldehyde group to form robust network structure [20]. This network restricts the flexibility of polymer chains, and in turn decreases the mobility of ions. Therefore, with the increase in heating temperature, the increase in degree of crosslinking density resulted in the decrease in conductivity. Besides, since the 'pathway' for ion movement may be much more severely disrupted or even blocked during the formation of network upon heating, compared to the other two samples, SPE with PEG$_{400}$ exhibits higher extent of reduction in conductivity at elevating temperatures.

3.5. Conductivity with ratio of [O]:[Li$^+$]

The conductivity of SPEs with mole ratio of [O]:[Li$^+$] at 2:1, 4:1, 6:1, 8:1, 10:1 and 12:1 corresponding to 88%, 57%, 38%, 28%, 23%, 19% (wt%) LiClO$_4$ of PVB, respectively by using 30 wt% PEG$_{400}$ of PVB as plasticizer is shown in Fig. 6; every data was obtained by averaging three measurements on each composition with an error of ±3%. The conductivity of the SPEs increases sharply with the addition of Li$^+$ content till a maximum conductivity is reached at around [O]:[Li$^+$] = 8:1; this can be attributed to the increase in the number of free ions resulted from the improvement in interaction of Li$^+$ with butyl segments together with plasticizing function provided by PEG$_{400}$ [7,11]. However, with the excessive addition of salt,
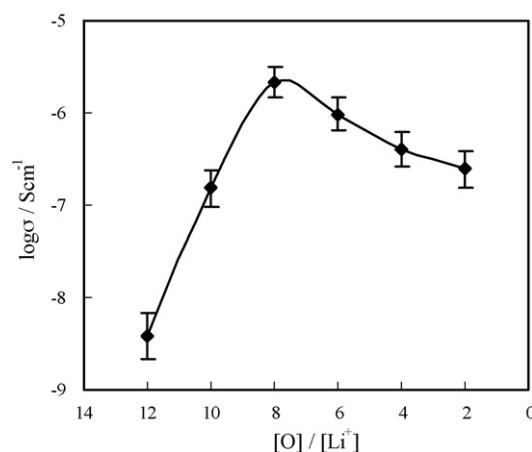

Fig. 5. Temperature dependence of DC conductivity (log σ) of PVB/LiClO$_4$ solid electrolyte films with PEG$_{200}$, PEG$_{400}$ and PEG$_{600}$ (30% of PVB) as plasticizers.

Fig. 6. Compositional (mole ratio of [O]/[Li$^+$]) dependence of conductivity (log σ) of PVB/LiClO$_4$ solid electrolyte films with 30% PEG$_{400}$ (wt% of PVB) as plasticizers.

some of $LiClO_4$ salt may exist as pair ion rather than free ion; more severely, if the salt content is high enough, some of the salt may aggregate together to form 'insulating island' as a separate phase which in turn restricts the mobility of free ions, in such a case the plasticizer alleviates or even loses its plasticizing function [21]. As such, for the purpose of achieving desired conductivity, the compositions of SPEs should be controlled properly at certain ratio of basic polymer with ionic salts.

3.6. XRD study

Fig. 7 shows the XRD analysis curves of (a) $LiClO_4$, (b) PVB, (c) $PVB/LiClO_4$, and (d) $PVB/LiClO_4/PEG_{400}$, respectively. Fig. 7(a) represents the characteristic diagram of $LiClO_4$ with crystalline nature. Fig. 7(b) showed that the chain stacks of PVB used in this study was mostly in amorphous states with broad hump at 2θ from $15°$ to $25°$ which represents the short distance sequential arrangements like most of other amorphous polymers [22]. When $LiClO_4$ was blended with PVB, all the corresponding 2θ angles of $LiClO_4$ shift to lower values and the intensity of the crystallinity also decrease as shown in Fig. 7(c), these correspond to the enlargement of crystal parameters and the disruption of the $LiClO_4$ crystal, resulted from the penetration of PVB chains in the crystalline regions of $LiClO_4$. When PEG_{400} was added in this blending matrix, all the crystal peaks of $LiClO_4$ disappear in Fig. 7(d), indicating that the crystal structure of $LiClO_4$ was changed to amorphous state. Simultaneously, the decrease in intensity of PVB hump suggests that the short distance sequential arrangements of PVB chains were also disturbed by the addition of PEG_{400} [6], resulting in the improvement in moving space for ions.

By properly selecting plasticizers and controlling their amount, the state of inorganic salt were changed from crystalline to amor-
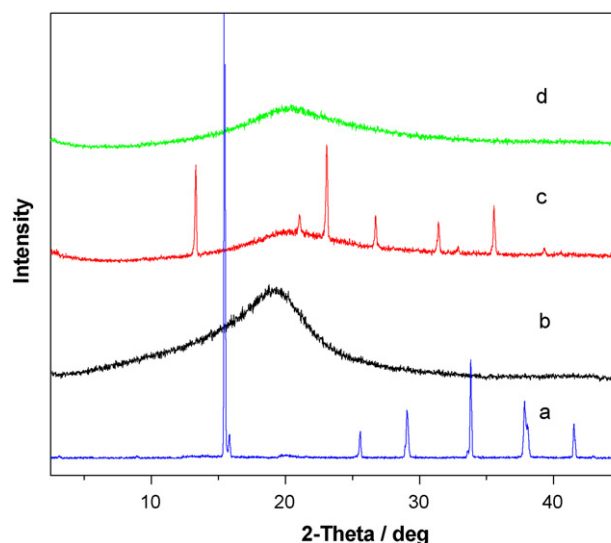

Fig. 7. XRD patterns of (a) $LiClO_4$, (b) PVB, (c) $PVB/LiClO_4$, and (d) $PVB/LiClO_4$ with PEG_{400} (30% of PVB).

phous state so that the mobility of ions in SPEs could be improved [23–25]; the sequential arrangements of the polymer chains could be disrupted so that the mobility of ions could be improved further, and in turn the conductivity of SPEs could be much more enhanced.

3.7. Surface morphologies

The surface morphologies of the solid electrolyte films for $PVB/LiClO_4$ (a), and $PVB/LiClO_4$ with PEG_{400} (wt% of PVB) at 20%
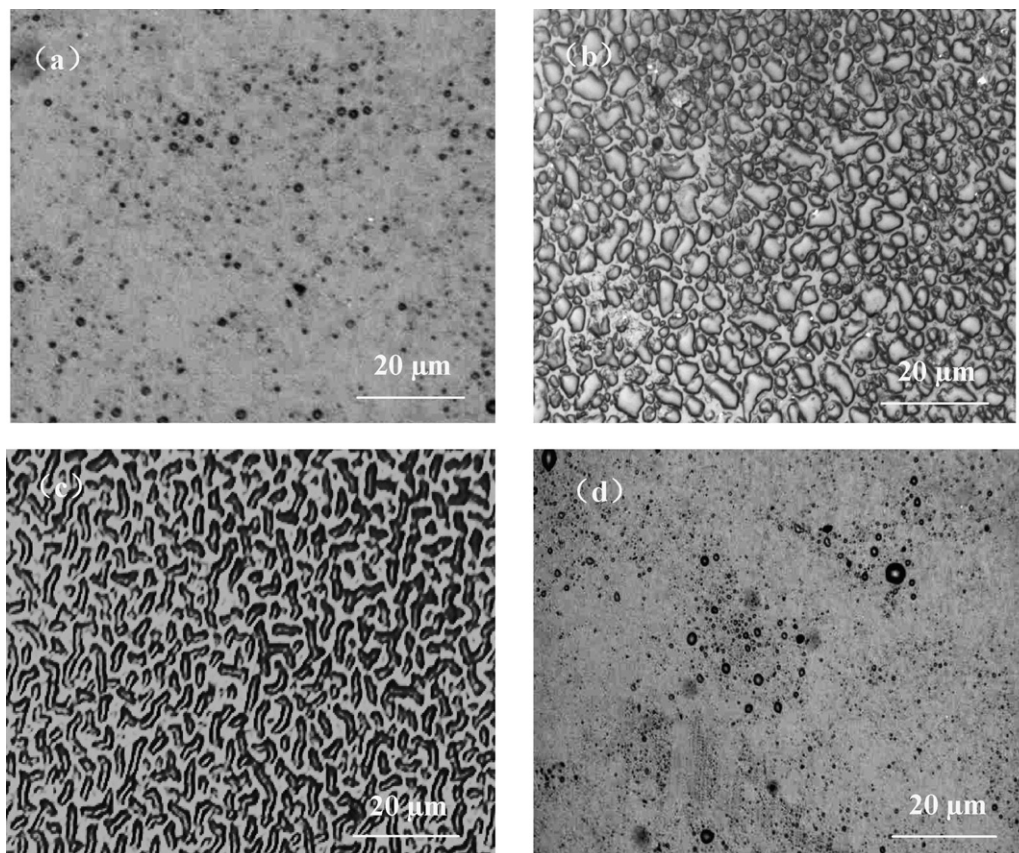

Fig. 8. Digital microscopy images of solid electrolyte films for $PVB/LiClO_4$ (a), and $PVB/LiClO_4$ with wt% PEG_{400} of PVB at 20% (b), 30% (c) and 50% (d), respectively.

(b), 30% (c) and 50% (d), respectively are shown in Fig. 8. The surface image obtained for PVB/LiClO$_4$ film (a) presents a constantly flatness morphology dotted with uneven aggregation of LiClO$_4$ salt. The mixed electrolyte film with 20% PEG (wt%) of PVB shows pebble design randomly distributed on the film surface (b); while the addition of PEG$_{400}$ at 30% (wt%) of PVB to the polymer electrolyte significantly changes its surface morphology to well-distributed grain design, the 'pebbles' in (b) were changed to slender worm-like pattern in (c). With the excessive addition of 50% PEG$_{400}$ (wt%) of PVB, its surface morphology (d) returned to a pattern similar to that in (a) except for the appearance of much lager dots, indicating the uneven aggregation of LiClO$_4$ salt, PVB or even PEG$_{400}$. It could be inferred that only in the surface in (c), the 'pathway' could be formed much effectively so that larger free moving space for ions were available [23–25] and hence this SPE exhibited conductivity superior to that of others in this study.

4. Conclusions

PVB/LiClO$_4$ polymer electrolyte films with PEG$_{200}$, PEG$_{400}$ and PEG$_{600}$ as plasticizers were prepared by solution-casting method. The bulk conductivities of the electrolyte films increased in the order of 10^{-10} to 10^{-6} S cm^{-1} as the addition of plasticizers. PEG$_{400}$ exhibited plasticizing function superior to PEG$_{200}$ and PEG$_{600}$, and the conductivity of the SPEs could reach 10^{-6} S cm^{-1} at room temperature by controlling the ratio of [O]:[Li$^+$] = 8 and adding 30% PEG$_{400}$ (wt%) of PVB. The conductivity of these SPEs exhibited strong dependence on the temperatures; at temperatures lower than 60 °C, the increase of conductivity with temperature exhibited linear Arrhenius relationships; while the decrease in conductivity with the increase in heating temperatures could be attributed to the crosslinking reaction among hydroxyl and aldehyde groups in PVB and PEG. The plasticizing function of PEG was found to change the state of inorganic salt from crystalline to amorphous state, increase the flexibility of PVB and also disturb the sequential arrangements of PVB polymer chains; these resulted in the improvement in moving space for ions in SPEs and even 'pathway' formation especially in SPE with PEG$_{400}$ at 30% (wt%) of PVB, and accordingly these resulted in the enhancement in the bulk conductivity.

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