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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.

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 $LiN(CF_3SO_2)_2$ or $LiCF_3SO_3$ 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*-hexafluoropropylene) 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