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Preparation and characterization of PVC–$LiClO_4$ based composite polymer electrolyte

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ABSTRACT

The preparation of PVC-$LiClO_4$ based composite polymer electrolyte was carried out to study the effect of ceramic fillers such as ZnO, TiO_2 and Al_2O_3 on the room temperature conductivity. The samples were tested using impedance spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The samples were prepared with different percentage (%) by weight of ceramic filler. The highest ionic conductivity achieved was $3.7 \times 10^{-7}\,S\,cm^{-1}$ for the sample prepared with 20% of ZnO. The glass transition temperature decreases with the fillers concentration due to the increasing amorphous state. While, the decomposition temperature increases with the increase in the fillers content. Both of these thermal properties influence the enhancement of the conductivity value. The morphology of the samples shows the even distribution of the ceramic filler in the samples however the filler starts to agglomerate in the sample at higher concentration of filler. In conclusion, the addition of ceramic filler improves the ionic conductivity of PVC-$LiClO_4$ composite polymer electrolyte.

1. Introduction

The role of filler in a solid polymeric electrolyte system is crucial as it serves as an agent to improve the conductivity of the electrolyte. There are two types of fillers that can be introduced in the electrolyte system, namely, organic molecule filler and inorganic molecule filler. The disadvantage of organic molecule filler such as propylene carbonate (PC) and ethylene carbonate (EC) is that they are more expensive compared with inorganic molecule filler. In Ref. [1], a solid polymeric electrolyte of PVC–$LiClO_4$ with the organic molecules filler of propylene carbonate (PC) has been used in a photoelectrochemical cells of ITO/TiO_2/PVC–$LiClO_4$/graphite as the medium for the redox reaction to take place. However, the ionic conductivity of the electrolyte at the operating temperature (40–50 °C) of the cells is still low ranging from 10^{-6} to $10^{-5}\,S\,cm^{-1}$. The photoelectrochemical cells performance such as the short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) strongly depend on the ionic conductivity of the electrolyte [2]. The small cells performance is due to the low conductivity of the electrolyte.

One way of improving the conductivity of the electrolyte is to introduce an inorganic compound filler such as SnO_2, SiO_2, Al_2O_3, and the organic molecules filler for replacing costly plasticizer such as ENR and dimethyl formamide (DMF) into the polymeric electrolyte system [3–9]. This filler promotes more free lithium ions and produce more amorphous regions in the electrolyte for the transfer of charge carriers. Therefore, the conductivity of the electrolyte could be improved. Another way of improving the conductivity of the solid polymeric electrolyte is to introduce the blend electrolyte system such as PVdF–HFP–PAN–$LiClO_4$ [10], PVdF–PVC–$LiBF_4$, PVdF–PVC–$LiClO_4$ [11], PEO–PBE–$LiClO_4$, PEO–PPO–$LiN(CF_3SO_2)_2$ [12] and PEO–PEGDME–$LiCF_3SO_3$ [13]. In this work, we prepared a solid polymeric electrolyte of PVC–filler–$LiClO_4$ with ZnO, Al_2O_3 and TiO_2 as filler. Ceramics filler was chosen as it is a cheaper material than PC filler. The objective of this work is to study the effect of filler concentration on the ionic conductivity of PVC–filler–$LiClO_4$ electrolyte.

2. Experimental

PVC (BDH Laboratory Reagent) low molecular weight with average M.W. approximately 100,000 and size of particle less than 0.250 mm were used. $LiClO_4$ salt was supplied by Alfa AeSar A. Johnson Malthey Company. Ceramic fillers used are ZnO (M.W. 81.4) supplied by M&B Laboratory Chemicals with grain sizes <100 nm and purity of 99.9%, TiO_2 (Sigma-Adrich) with grain sizes <5 μm and purity of 99.9%, and Al_2O_3 by laboratory

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reagents with grain sizes $<5\,\mu m$ and purity of 99.9%. Six grams of PVC was dissolved into 100 ml THF and stirred using a magnetic stirrer to form a homogenous solution. Then, 1.8 g of $LiClO_4$ was added into the solution. About 5 wt % of ceramics filler was then added into the solution and the mixtures were then stirred for 24 h and then poured into a petri dish and left for slow drying to room temperature to form the electrolyte films. The dried films were obtained after THF solvent completely evaporated. The films were then peeled off from the dish. These steps were repeated for preparing PVC–filler–$LiClO_4$ with 10, 15, 20 and 25 wt% filler (ZnO, Al_2O_3, TiO_2). The films with thickness of 0.2–0.5 mm were kept in a desiccator for further use. The samples were further dried in a vacuum oven before undergoing impedance spectroscopy DSC, TGA and SEM testing. Conductivity measurements were performed by sandwiching the electrolyte films between two stainless steel electrodes and mounted onto holder. The scanning frequencies range from 100 Hz to 1 MHz using high frequency resonance analyzer (HFRA) model 1255. Initially, the film samples were cut into a shaped disc with a diameter of 16 mm. The impedance measurements were conducted at room temperature.

3. Results and discussion

Fig. 1 shows the effect of different inorganic fillers in composite polymer electrolyte (CPE) PVC–$LiClO_4$ system at room temperature. The average ionic conductivity for PVC–$LiClO_4$ without filler is around $10^{-9}\,S\,cm^{-1}$ and it was also observed that the conductivity varies with the concentration and type of inorganic filler. The ionic conductivity of CPE of PVC–$LiClO_4$ with TiO_2 and Al_2O_3 fillers increased gradually with the increasing of fillers content, while the conductivity of PVC–$LiClO_4$ with ZnO decrease after the optimum level of filler content at 20 wt%. The highest ionic conductivity is $3.7\times10^{-7}\,S\,cm^{-1}$ obtained at 20 wt% of the addition of ZnO. The ionic conductivity of PVC–$LiClO_4$ with TiO_2 and Al_2O_3 fillers were slightly lower than the ionic conductivity of PVC–$LiClO_4$ with ZnO. The highest room temperature ionic conductivity of PVC–$LiClO_4$ with TiO_2 is $4.4\times10^{-9}\,S\,cm^{-1}$ obtained at 25 wt% TiO_2 [14]. It is lower than the electrolyte with ZnO filler by 84 times. The highest room temperature ionic conductivity of PVC–$LiClO_4$ with Al_2O_3 is $3.4\times10^{-10}\,S\,cm^{-1}$ obtained at 16 wt% Al_2O_3 [15]. It is lower than the electrolyte with ZnO filler by 1088 times. These phenomena can be explained by the number of interaction occurring between lithium ion (Li^+) and oxygen atom (O). The inorganic filler with the presence of oxygen atom or specifically the lone pair of electron in the oxygen structure contribute to coordination bond with Li^+ [16]. The presence of the electron pair in the oxygen structure increase twice in TiO_2 compared with ZnO and triple in Al_2O_3 filler. Thus, the effective interactions between Li^+ and $O^{\delta-}$ in different inorganic fillers decrease proportional to the increasing of $O^{\delta-}$ in CPE PVC–$LiClO_4$ system. The same interaction occurs in PVC and lithium salts because PVC also contains lone pair of electron in chlorine structure [17]. The presence of inorganic fillers could results in a greater number of ion dissociation, which produces a greater number of charge carries for ionic transport [8] and reduces the number of ion pairing in the electrolyte [18]. The other ways of enhancing the conductivity by the introduction of inorganic fillers are the presence of the amorphous regions and the reduction of crystalline regions of CPE. The introduction of inorganic fillers into CPE system will make the electrolyte more amorphous and promote more free Li^+ from the organic salt of $LiClO_4$ for the charge transfer in the electrolyte [14]. The relationship between the conductivity and the amorphous phase was expressed in terms of the decrement of glass transition temperature (T_g) obtained from DSC thermographs and illustrated in Fig. 2.

The addition of inorganic filler of ZnO into the PVC–$LiClO_4$ system shows the unchanging T_g. It can be concluded that the T_g of the CPE PVC–$LiClO_4$ is not influenced by the addition of ZnO filler. However, the addition of inorganic filler of TiO_2 shows two of the apparent peaks. The first peak at 54 °C represents T_g of PVC which is sharp and broad. It was reported that T_g of pure PVC is around 51 °C [19]. While, the second peak refers to T_g of complex PVC–$LiClO_4$–TiO_2. The T_g for CPE PVC–$LiClO_4$ with TiO_2 and Al_2O_3 decrease with the increasing of weight (%) of inorganic fillers due to the increasing of the amorphous state [14,15]. These results may support the effect of inorganic fillers on the increasing of ionic conductivity in the system of PVC–$LiClO_4$–TiO_2 and PVC–$LiClO_4$–Al_2O_3. It was reported that the TiO_2 and Al_2O_3 addition influenced the polymer crystal formation as the inorganic fillers such as $LiAlO_2$ and Sm_2O_3 decrease the crystalline phase of polymer electrolyte such as PEO and PVdF [18,20–24]. The decrement of T_g also shows the increment in segmental motion backbone. The inorganic fillers reduced the crystalline regions [14,15,20–25] and produce more space for the atoms, molecules and the segment chain to transport in the system [26]. In Ref. [10], it is suggested that the complicated, acid–base interactions between Li^+ and ClO_4^- in salt, titanium, oxygen in TiO_2 and fluorine in PVdF occur with the addition of TiO_2 into the PVdF–$LiClO_4$ system. Such interactions can not only induce structural modification of the polymer chain, which provides a favorable conduction path for faster migration of Li ions on the

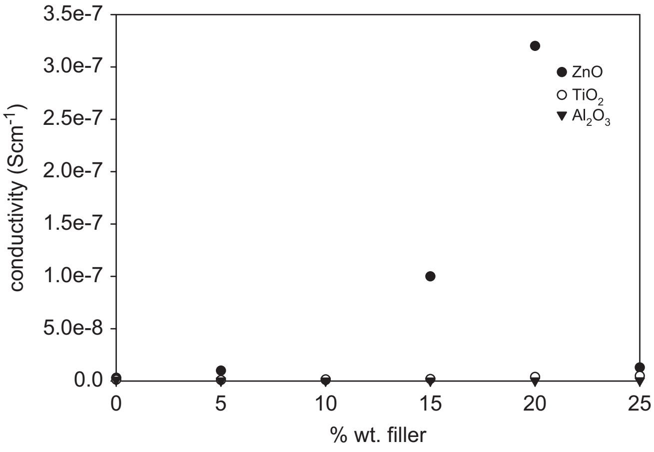

Fig. 1. Variation of room temperature conductivity with filler content.

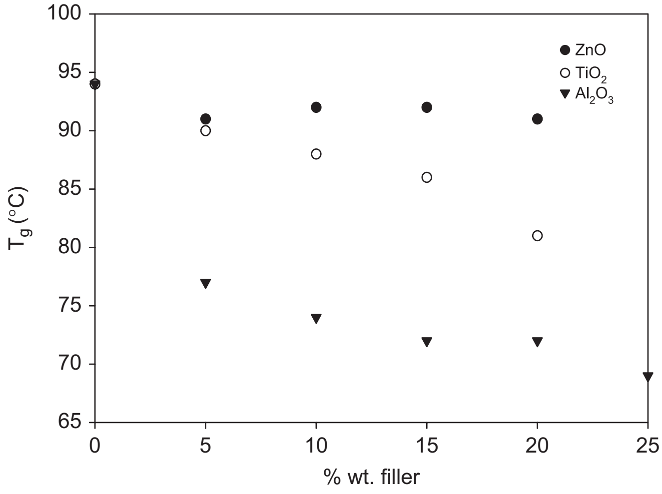

Fig. 2. Variation of glass transition temperature with filler content.