THE EFFECT OF DIFFERENT WEIGHT PERCENTAGES OF LEAD (II) OXIDE NANOPARTICLES BASED SOLID POLYMER ELECTROLYTE TOWARDS IONIC CONDUCTIVITY

[1]MEE YOKE CHONG, [2]ARSHID NUMAN, [3]K. RAMESH, [4]S. RAMESH

[1,2,3,4]Centre of Ionics University of Malaya, Department of Physics, Faculty of Science , University of Malaya, 50603 Kuala Lumpur, Malaysia
[1]Faculty of Information, Technology, Mathematics and Science, INTI International University, Persiaran Bandar Baru Nilai, 71800 Nilai, Malaysia
E-mail: [1]rameshtsubra@gmail.com, [2]meeyoke.chong@newinti.edu.my

---

Abstract- The solid polymer electrolyte (SPE) film based on hydroxylethyl cellulose, magnesium triflate, 1-ethyl-3-methylimidazolium and lead(II) oxide nanoparticles was prepared by solution casting technique. The SPE formed exhibits low ionic conductivity at room temperature, hence various weight percentages (1%, 2%, 3% and 4%) of lead(II) oxide nanoparticles is incorporated into the SPE to enhance the conductivity. By conductivity studies it revealed that the maximum ionic conductivity of 4.99×10^{-4} S cm^{-1} is achieved for SPE with 3 wt. % of lead(II) oxide nanoparticles at room temperature. All the SPEs obeyed Arrhenius theory.

Keywords- Biodegradable, Ionic conductivity, Lead(II) oxide, Nanoparticles, Solid polymer electrolyte.

I. INTRODUCTION

Biodegradable host polymers have been studied as one type of sustainable candidate in solid polymer electrolyte (SPE) owing to the global warming and the blooming of the fossil fuel crisis. Hydroxylethyl cellulose (HEC) has been chosen in this study due to its biodegradable properties. It has been widely used in pharmaceutical and food industry. [1] SPEs allured huge amount of attention due to their fantastic applications in energy storage devices because they possess good thermal stability, flexible, easy at handling and fabrication and good contact at interface with working electrodes. [2–4] However, the low ionic conductivity at room temperature hinders their commercialization. Thus, various attempts were introduced (such as blending polymer with amorphous polymers, crosslinking polymers, incorporation of ionic liquids and doping of either inorganic nanoparticles or organic solvents) to mitigate the problem. [5–6] Two methods were adopted in this study in order to enhance its conductivity, which are incorporation of nanoparticles and ionic liquids.

Lead(II) oxide (PbO) nanoparticles were used in this study because it is one of the semiconductors which possess fundamental size-dependent optoelectronic properties and their wide range of applications. [7] It has been widely used as network modifiers in luminescent glassy materials, storage batteries, gas sensors, pigments and nanoscale electronic devices. [7–10] Additionally, doping of nanoparticles maximize the adsorption of electrolyte through their porous structure and minimize the chance of leakage. [3,6] Moreover, the reactive groups on the nanoparticles improves the properties (ionic conductivity and mechanical strength) of the nanoparticles-based SPE. [11] The ionic conductivity of the solid polymer electrolyte can be further enhanced by incorporating the ionic liquids. Hence, 1-ethyl-3-methylimidazolium ionic liquid was incorporated in this study because of its non-volatile, non-flammable, electrochemical stability, wide electrochemical window and high ionic conductivity. [12]

II. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

Hydroxylethyl cellulose (HEC), magnesium trifluoromethanesulfonate ($MgTf_2$), lead(II) oxide (PbO) nanoparticles (25–30 nm) and 1-ethyl-3-methylimidazolium (EMIMTf) were purchased from Sigma–Aldrich, USA. PbO nanoparticles were activated in accordance with the method reported by Taghizadeh M.T. and Aghjekohal P.S. before use. [1] HEC and $MgTf_2$ were pre-heated at 100 °C for 1 hour in order to remove the moisture. In the preparation of SPE, different weight percentages of HEC, $MgTf_2$, EMIMTf and PbO nanoparticles were dissolved in deionized water. The solution was sonicated for 30 minutes followed by continuous stirring for 24 hours at room temperature. The solution was then casted on Teflon coated aluminium foil and was allowed for evaporation under 70 °C for 24 hours. An opaque, thin film was obtained. The opaqueness of the SPEs increased with the amount of PbO nanoparticles as shown in Fig. 1. The designation and compositions of the SPEs are given in Table 1.

Table 1: Designation and compositions of SPE

Designation	Compositions of HEC:$MgTf_2$:EMIMTF:PbO
P0	48.0: 12.0: 40: 0
P1	47.2: 11.8: 40: 1
P2	46.4: 11.6: 40: 2
P3	45.6: 11.4: 40: 3
P4	44.8: 11.2: 40: 4

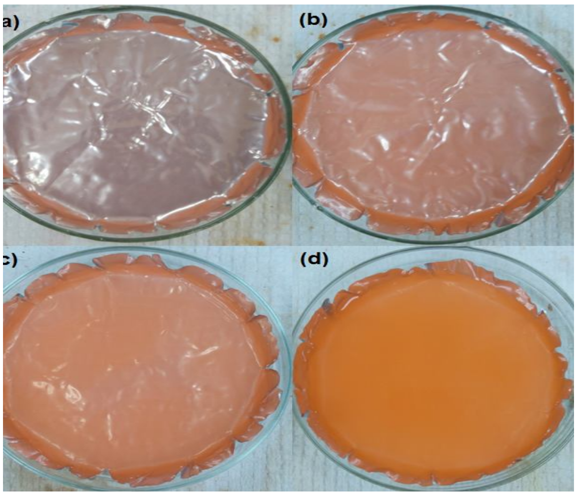

Fig. 1: The opaqueness level of (a) P1 (b) P2 (c) P3 and (d) P4

2.2. Characterizations

The thickness of the film was measured using Mitutoyo micrometer screw gauge. Ionic conductivity measurement was performed by using HIOKI 3532-50 LCR HiTESTER, over a frequency range between 50 Hz and 5 MHz at different temperatures. Samples were mounted on the holder with stainless steel (SS) blocking electrodes under spring pressure with the configuration of SS/SPE/SS blocking electrodes. The conductivity-temperature study was conducted in the temperature range of 25–120 °C.

III. RESULTS AND DISCUSSION

3.1. Ionic conductivity

The electrical properties of SPE complexes with different weight percentages of PbO nanoparticles were analyzed by impedance spectroscopy. The ionic conductivity (σ) of the SPE was evaluated according to formula: [2]

$$\sigma = d/(R_b \times A) \qquad (1)$$

where R_b is the bulk resistance; d is the film thickness and A is the effective area of the electrode.

Fig. 2 depicts the evaluated Cole-Cole plot of SPEs (with and without PbO nanoparticles) at room temperature. When the content of PbO nanoparticles was increased from 1 to 3 wt. % into P0, the real part impedance (Z') decreased as shown in inset of Fig. 2. It indicates that the ionic conductivity increased from P0 to P3 (as illustrated in Fig. 3) resulted from the adsorption of Mg^{2+} ions on the host polymer. Mg^{2+} ions were readily to adsorb on the host polymer because the salt dissociates easily due to the large size of anion. Similarly, the transportation of Mg^{2+} ions was also eased by the presence of partially positive and negative charge on PbO nanoparticles which minimized the formation of intermolecular hydrogen bonding among the polymer chains. Thus, the recrystallization of host polymer was prevented. [3] When the contents of PbO nanoparticles were increased to 4 wt. %, the Z' increased due to the aggregation of nanoparticles. Hence, higher amounts of nanoparticles decreased the charge carrier kinematics due to blocking phenomenon. [4]

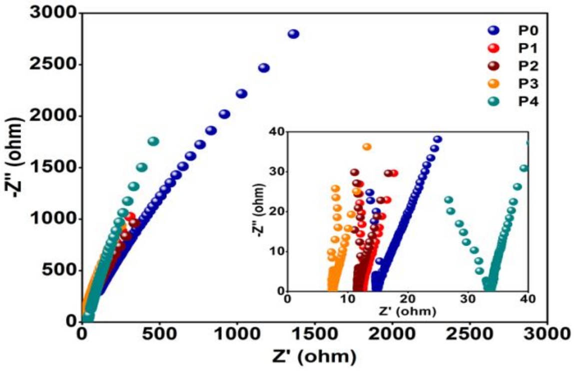

Fig. 2: Cole-Cole plot of the SPEs (with and without PbO nanoparticles) and inset is the enlarged view of the measured Cole-Cole plot

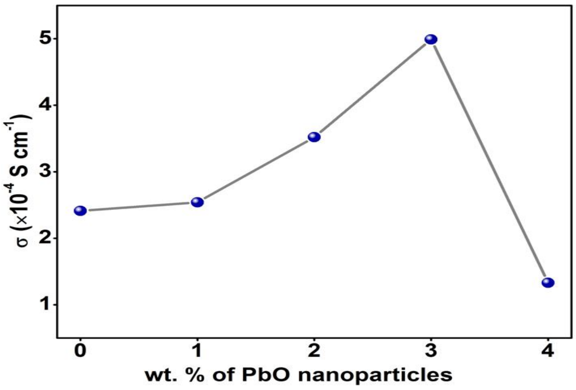

Fig. 3: Ionic conductivities at different wt. % of PbO nanoparticles at room temperature

Fig. 4 describes the temperature dependent ionic conductivities of SPEs (with and without PbO nanoparticles). The ionic conductivities for all SPEs are directly proportionate to the absolute temperature with regression values (R^2) close to unity, which means that SPE obeyed Arrhenius theory. It can be explained by free volume model, in which the expansion of host polymer upon heating provides more space for transportation of mobile carriers. Additionally, the mobility of charge carriers was enhanced when the temperature was increased. Hence the mobility of charge carriers were able to overcome the energy barrier to the segmental movements of the SPE. [4]

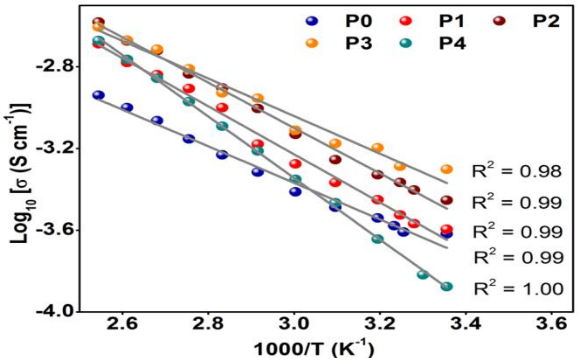

Fig.4:Temperature dependence ionic conductivities for SPEs (with and without PbO nanoparticles)

CONCLUSIONS

Solution casting technique was used to prepare the SPEs and they were evaluated by doping it with different wt. % of PbO nanoparticles. Impedance spectroscopy was used to measure the ionic conductivities of the SPEs upon addition of PbO nanoparticles. It was found that P3 achieved highest ionic conductivity (4.99×10^{-4} S cm^{-1}) at room temperature. All SPEs obeyed Arrhenius theory.

ACKNOWLEDGMENTS

The authors would like to thank MyPhD for their scholarship, Universiti Malaya Research Grant IPPP (Project Account Number: PG030-2015A) and INTI International University, Nilai for their technical support.

REFERENCES

[1]. Taghizadeh, M.T.; Aghjekohal, P.S., “Sonocatalytic degradation of 2-hydroxyethyl cellulose in the presence of some nanoparticles”, Ultrasonics Sonochemistry, 2015, 26, 265–272.

[2]. Y. Ma, L. B. Li, G. X. Gao, X. Y. Yang, J. You, P. X. Yang, “Ionic conductivity enhancement in gel polymer electrolyte membrane with N-methyl-N-butyl-piperidine-bis(trifluoromethylsulfonyl)imide ionic liquid for lithium ion battery”, Colloids and Surface A: Physiochem. Eng. Aspects, vol.502, pp. 130–138, 2016.

[3]. D. Praveen, S. V. Bhat, R. Damle, “Role of silica nanoparticles in conductivity enhancement of nanocomposite solid polymer electrolytes:(PEGx NaBr): ySiO$_2$”, Ionics, vol. 19, pp. 1375–1379, 2013.

[4]. M. I. H. Sohaimy, M. I. N. Isa, “Effect of Ammonium Carbonate Salt Concentration on Structural and Ionic Conductivity of Cellulose Based Solid Polymer Electrolytes”, Fibers and Polymers, vol.16, pp. 1031-1034, 2015.

[5]. M. L. Yong, D. H. Ko, J. Y. Lee, J. K. Park, “Highly ion-conductive solid polymer electrolytes based on polyethylene non-woven matrix”, Electrochimica Acta, vol.52, pp.1582–1587, 2006.

[6]. D. Kumar, S. A. Hashmi, “Ion transport and ion-filler polymer interaction in poly(methylmethacrylate)-based, sodium ion conducting, gel polymer electrolytes dispersed with silica nanoparticles”, Journal of Power Sources, vol.195, pp.5010–5108, 2010.

[7]. 7. A. Aliakbari, E. Najafi, M. M. Amini, S. W. Ng, “Structure and photoluminescence properties of lead(II) oxide nanoparticles synthesized from a new lead(II) coordination polymer”, Monatsh Chem, vol.145, pp. 1277–1285, 2014.

[8]. 8. P. B. Taunk, R. Das, D. P. Bisen, R. K. Tamrakar, “Optical and

[9]. Structural characterization of pure and zinc-doped lead oxide nanostructures synthesized by chemical root method”, Optik, vol.127, pp. 6028–6035, 2016.

[10]. 9. I. Kashif, A. A. El-Maboud, R. El-said, E. M. Sakr, A. A.

[11]. Soliman, “The role of lead oxide on structural and physical

[12]. properties of lithium diborate glasses”, Journal of Alloys and Compounds, vol.539, pp.124–128, 2012.

[13]. 10. A. Shahrjedi, S. S. H. Davarani, E. Najafi, M. M. Amini, “Sonochemical synthesis of a new nano lead(II) complex with quinolone-2-carboxylic acid ligand: A precursor to produce pure phase nano-sized lead(II) oxide”, Ultrasonics Sonochemistry,vol.22, pp. 382-390, 2015.

[14]. 11. G. Dimitrios, Papageorgiou, K. Chrissafis, E. Pavlidou, E. A. Deliyanni, Z. George, Z. Terzopoulou, D. N. Bikiaris, “Effect of nanofiller’s size and shape on the solid state microstructure and thermal properties of poly(butylene succinate) nanocomposites”, Thermochimica Acta, vol.590, pp. 181–190, 2014.

[15]. 12. M. Y. Chong, C. W. Liew, A. Numan, K. Yugal, K. Ramesh, H. M. Ng, T. V. Chong, S. Ramesh, “Effects of ionic liquid on the hydroxylpropylmethyl cellulose (HPMC) solid polymer electrolyte”, Ionics, DOI 10.1007/s11581-016-1768-0, 2016.

★★★