Advanced Materials Research *Online: 2013-11-21*
ISSN: 1662-8985, Vol. 832, pp 224-227
doi:10.4028/www.scientific.net/AMR.832.224
© 2014 Trans Tech Publications, Switzerland

Effect of Filler Type on the Electrical Properties of Hexanoyl Chitosan-Based Polymer Electrolytes

Nurul Hazwani Aminuddin Rosli[1, a], Fadiatul Hasinah Muhammad[2,b], Chan Chin Han[1,c] and Tan Winie[1,d]

[1]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia

[2]Pusat Asasi, Universiti Teknologi MARA, 42300 Puncak Alam, Malaysia

[a]wani_pearl@yahoo.com, [b]fadiatul@salam.uitm.edu.my, [c]cchan@salam.uitm.edu.my, [d]tanwinie@salam.uitm.edu.my

Keywords: Hexanoyl Chitosan, $LiClO_4$, TiO_2, SiO_2, Rice and Roth Model

Abstract. A preliminary investigation of polymer electrolyte based on hexanoyl chitosan, lithium perchlorate ($LiClO_4$) and various filler additives are described in this paper. Hexanoyl chitosan-based nanocomposite polymer electrolytes were prepared using solution casting technique. The effect of filler addition and type of filler on the electrical properties of the prepared electrolyte system was investigated by impedance spectroscopy (IS). The maximum conductivity of 3.06×10^{-4} S cm^{-1} and 1.96×10^{-4} S cm^{-1} were achieved for the hexanoyl chitosan-$LiClO_4$-TiO_2 and hexanoyl chitosan-$LiClO_4$-SiO_2 electrolyte system, respectively. The variations in conductivity observed were discussed quantitatively using the Rice and Roth model from which the concentration of free ions and their mobility were calculated.

Introduction

Polymeric electrolytes have attracted considerable interest due to their potential application in solid state batteries, fuel cells and electrochromic devices [1-3]. The advantages of using solid polymer electrolytes (SPEs) are concentrated on their desirable characteristics: good compatibility with lithium metal, non-leakage, easy processing and continuous production, low self-discharge in batteries and so on [4]. However, the major drawback of SPEs is low ionic conductivity at ambient temperature. To enhance the ionic conductivity of SPEs, several approaches are suggested such as blending, addition of filler and plasticization.

The addition of filler such as Al_2O_3, TiO_2 and SiO_2 increases the conductivity and mechanical properties of the polymer system. The addition of filler to the polymer-salt complexes helps in lowering the glass transition temperature, T_g of polymer by increasing the volume fraction of the amorphous phase [5,6]. The decrease of T_g improve the segmental flexibility of polymer chains which leads to the increase in mobility of conducting ions and hence conductivity enhancement.

In this paper, the effect of filler addition and type of filler on the electrical properties of hexanoyl chitosan-based polymer electrolytes will be investigated and discussed.

Experimental Procedure

Lithium perchlorate ($LiClO_4$) purchased from Fluka AG. Ttitanium oxide (TiO_2) (particle size ~30-40 nm) and silica oxide (SiO_2) (particle size ~30 nm) obtained from Nanostructured & Amourphous Material Inc were used as the inorganic filler without any treatment and surface modification. Tetrahydrofuran (THF) with purity > 99% from J.T. Baker was used as the solvent. Films of hexanoyl chitosan-based polymer electrolyte were prepared by the solution casting technique. To prepare the nanocomposite polymer electrolytes, the required amount of TiO_2 or SiO_2 was added to hexanoyl chitosan and $LiClO_4$ dissolved in THF. The mixture was stirred at room temperature until TiO_2 or SiO_2 particles are dispersed homogenous before casting into separate glass petri dishes. They are left to evaporate at room temperature for the films to form. The films were then kept in a dessicator for further drying.

All rights reserved. No part of contents of this paper may be reproduced or transmitted in any form or by any means without the written permission of Trans Tech Publications, www.ttp.net. (#69792858, Pennsylvania State University, University Park, USA-17/09/16,00:14:34)

The impedance measurement of the films was carried out using HIOKI 3532-50 LCR Hi Tester in the frequency range of 100 Hz to 1 MHz. The films were sandwiched between two stainless steel electrodes with diameter 1 cm under spring pressure. The conductivity can be calculated using equation:

$$\sigma = \frac{t}{R_b A} \tag{1}$$

where t is the thickness of the sample and A is the area of contact between the electrode and the sample. The bulk impedance, R_b was obtained from the cole-cole plot of negative imaginary versus real impedance.

Results and Discussion

The hexanoyl chitosan-$LiClO_4$ complexes exhibit ionic conductivity of 1.83×10^{-5} S cm^{-1}. An enhancement in the ionic conductivity has been found on filler addition. The room temperature conductivity achieved with addition of 6 wt.% TiO_2 and SiO_2 is 3.06×10^{-4} S cm^{-1} and 1.96×10^{-4} S cm^{-1}, respectively. It is important to note here that the composite electrolyte system contained the fixed amount of hexanoyl chitosan and $LiClO_4$. Fig. 1 shows the frequency dependence of dielectric constant, ε_r for the prepared polymer electrolytes. At low frequency, the filler-added electrolyte systems have higher dielectric constant as compared to filler-free system with the TiO_2-added system exhibits highest value of dielectric constant. In our previous work [7], we discussed that the dielectric constant is a measure of the number of Li^+ cations. The increase in dielectric constant represents the increase in the number of Li^+ cations. Hence, it is shown that the variation in conductivity for filler-free and filler-added electrolyte system is due to the variation in the number of available free Li^+ cations.

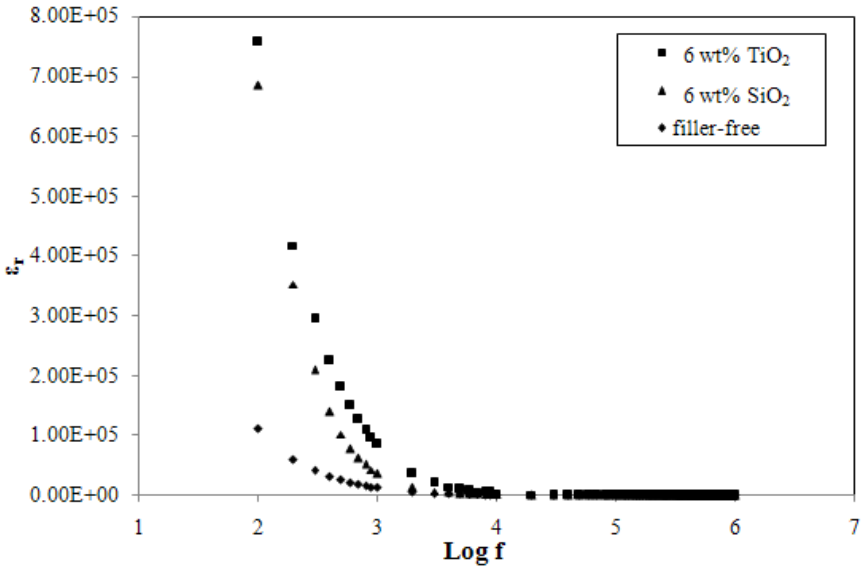

Fig. 1, Frequency dependence of dielectric constant, ε_r for filler-free, TiO_2 or SiO_2-added hexanoyl chitosan-based polymer electrolytes at room temperature.

In order to analyze quantitatively the conductivity behaviour observed, the number of free ions, n has been calculated based on the Rice and Roth model [8]. Knowing n, the mobility of free ions, μ can be calculated based on:

$$\sigma = en\mu \tag{2}$$

The calculated values of n and μ for the prepared nanocomposite electrolyte system are presented in Table 1.

Table 1, Transport parameters for hexanoyl chitosan-based polymer electrolytes

Electrolyte System	σ_{RT}, (S cm^{-1})	E_A (eV)	n (cm^{-3})	μ (cm^{2}V^{-1}s^{-1})
Hexanoyl chitosan-$LiClO_4$	1.83×10^{-5}	0.120	3.48×10^{18}	3.34×10^{-5}
Hexanoyl chitosan-$LiClO_4$-TiO_2	3.06×10^{-4}	0.075	8.39×10^{18}	2.28×10^{-4}
Hexanoyl chitosan-$LiClO_4$-SiO_2	1.96×10^{-4}	0.117	3.66×10^{18}	1.35×10^{-4}

It is apparent from the table that the increase of conductivity with filler addition is due to the higher number of free Li^+ ions and its mobility. The roles of filler as the conductivity enhancer are [9]: (i) helps the dissociation of the lithium salt which generates greater numbers of Li^+ cations by Lewis acid-base interactions between the filler surface, ionic species and electron donor atoms of hexanoyl chitosan and (ii) increases the mobility of Li^+ cations by providing conducting pathways at the filler surfaces.

Higher conductivity enhancement is brought about by TiO_2 addition as compared to SiO_2. This is because the more acidic nature of TiO_2 [10] promotes greater degree of salt dissociation. The $CF_3SO_3^-$ anions dissociated from the salt can interact with the filler surface acid groups via transient hydrogen bonding [9]. The TiO_2 provides more surface acid groups for complexation with $CF_3SO_3^-$ anions. This consequently reduces the re-association degree of Li^+ cations and $CF_3SO_3^-$ anions and thus allows greater number of Li^+ cations for ionic conduction.

Conclusion

An enhancement in the ionic conductivity of hexanoyl chitosan-$LiClO_4$ polymer electrolyte has been found on filler addition. Higher conductivity enhancement is brought about by TiO_2 as compared to SiO_2. Conductivity enhancement is caused by the increase in the concentration and mobility of free ions.

Acknowledgement

The authors wish to thank Ministry of Higher Education Malaysia for supporting this work through grant RACE 16/6/2 (4/2012).

References

[1] M. Watanabe, H. Uchida, M. Emori, Polymer electrolyte membranes incorporated with nanometer-size particles of Pt and/or metal oxides: Experimental analysis of the self humidification and suppression of gas-crossover in fuel cells, J. Phys. Chem. B 102 (1998) 3129-3137.

[2] H.Y. Sung, Y.Y. Wang, C.C. Wan, Preparation and characterization of poly(vinyl chloride-co-vinyl acetate)-based gel electrolytes for Li-ion batteries, J. Electrochem. Soc. 145 (1998) 1207-1211.

[3] M.A.K.L. Dissanayake, R. Frech, Infrared spectroscopic study of the phases and phase transitions in poly(ethylene oxide) and poly(ethylene oxide)-lithium trifluoromethanesulfonate complexes, Macromolecules 28 (1995) 5312-5319.

[4] W. Xu, Z.H. Deng, X.Z. Zhang, G.X. Wan, The influence of the compatibility of plasticizers with polymer ionic conductors on ionic conduction, J. Solid State Electrochem. 2 (1998) 257-261.

[5] Z. Li, G. Su, D. Gao, X. Wang, X. Li, Effect of Al_2O_3 nanoparticles on the electrochemical characteristics of P(VDF-HFP)-based polymer electrolyte, Electrochim. Acta 49 (2004) 4633-4639.

[6] H.M.J.C. Pitawala, M.A.K.L. Dissanayake, V.A. Seneviratne, Combined effect of Al_2O_3 nano-fillers and EC plasticizer on ionic conductivity enhancement in the solid polymer electrolyte $(PEO)_9LiTf$, Solid State Ionics 178 (2007) 885-888.

[7] Tan Winie, A.K. Arof, Transport properties of hexanoyl chitosan-based gel electrolyte, Ionics 12 (2006) 149-152.

[8] M.J. Rice, W.L. Roth, Ionic transport in super ionic conductors: a theoretical model, J. Solid State Chem. 4 (1972) 294-310.

[9] P.A.R.D. Jayathilaka, M.A.K.L. Dissanayake, I. Albinsson, B.-E. Mellander, Effect of nano-porous Al_2O_3 on thermal, dielectric and transport properties of the $(PEO)_9LiTFSI$ polymer electrolyte system, Electrochim. Acta 47 (2002) 3257-3268.

[10] S.H. Chung, Y. Wang, L. Persi, F. Croce, S.G. Greenbaum, B. Scrosati, E. Plichta, Enhancement of ion transport in polymer electrolytes by addition of nanoscale inorganic oxides, J. Power Sources 97-98 (2001) 644-648.