



Material Science and Engineering Technology IX

Material Science and Engineering Technology IX

Selected peer-reviewed full text papers from the 9th ICMSET, the 9th ICNNN and the 5th ICMTA

Edited by
Prof. Ramesh K. Agarwal



ISBN: 978-3-0357-1784-6

Materials Science Forum Vol. 1023

Electronically available at www.scientific.net

Prof. Ramesh K. Agarwal



TTP TRANS TECH PUBLICATIONS



Gel-Polymer Electrolytes for Sodium Batteries - Raman and Electrochemical Impedance Spectroscopic Studies

G. Menisha^{1,2,a}, J.H.T.B. Jayamaha^{1,b}, K. Vignarooban^{1,c*}, G. Sashikesh^{3,d}
K. Velauthamurthy^{3,e}, H.W.M.A.C. Wijayasinghe^{4,f} and M.A.K.L. Dissanayake^{4,g}

¹Department of Physics, University of Jaffna, Jaffna 40000, Sri Lanka

²University College of Jaffna, 29 Brown Road, Jaffna 40000, Sri Lanka

³Department of Chemistry, University of Jaffna, Jaffna 40000, Sri Lanka

⁴National Institute of Fundamental Studies, Hantana Road, Kandy 20000, Sri Lanka

^agmenisha@ucj.ac.lk, ^bjayamahatb@gmail.com, ^{c*}vigna@univ.jfn.ac.lk, ^dsashikesh@univ.jfn.ac.lk,
^ekvels@univ.jfn.ac.lk, ^fathula.wi@nifs.ac.lk, ^glakshman.di@nifs.ac.lk

Keywords: Sodium-ion batteries, gel-polymer electrolytes, electrochemical impedance spectroscopy, ionic conductivity and Raman spectroscopy

Abstract. Sodium-ion batteries (SIBs) as low-cost alternatives to expensive lithium-ion batteries become a hot R&D topic in the recent days due to the natural abundancy of sodium in the Earth's crust and also in the oceans. As far as solid electrolytes for SIBs are concerned, larger size of Na⁺ ions compared to that of Li⁺ ions hinders the ionic mobility resulting to insufficient ionic conductivity for practical applications. Development of quasi-solid state gel-polymer electrolytes (GPEs) would be a feasible solution to overcome this challenge. In this work, we developed Poly (methyl methacrylate) (PMMA) based GPEs with six different compositions dissolved in EC:PC (ethylene carbonate and propylene carbonate, 1:1 wt%) mixture. Among six different GPE samples investigated by Electrochemical Impedance Spectroscopic (EIS) and Raman Spectroscopic techniques, the best ambient temperature ionic conductivity of 4.2 mS cm⁻¹ was obtained for 9PMMA:9NaPF₆:41EC:41PC (wt%). Variation of ionic conductivity with inverse temperature showed Arrhenius behavior with almost constant activation energies. The best conducting GPE showed an activation energy of 0.14 eV. In the Raman spectra, very sharp crystalline peaks (400-850 cm⁻¹ wave number range) of NaPF₆ disappear in the gel state of the electrolytes confirming the non-crystalline nature of the GPEs. Boson modes remain almost constant in intensity for all the six different compositions. The best conducting GPE seems to be highly suitable for practical applications in SIBs as it has sufficient ambient temperature ionic conductivity.

Introduction

Lithium-ion batteries (LIBs) are the topmost choice for applications in portable electronic devices as well as in electric vehicles, especially due to their higher energy density and several other advantages. However, prices of lithium raw materials keep on increasing from the time of first commercialization of LIBs in 1991, mainly due to the limited availability of global lithium deposits and huge amount of consumption. Secondary battery chemistries beyond lithium-ion, such as sodium-ion batteries (SIBs), have been intensively investigated these days because of the natural abundancy of sodium raw materials [1-2]. Larger size of Na⁺ ions hinders the ionic mobility and hence synthesis of electrolytes with reasonably good ambient temperature ionic conductivity is one of the prime challenges as far as the development of SIBs are concerned. Reasonably good ambient temperature ionic conductivities would be expected in quasi-solid state GPEs, which facilitate the increased mobility of ionic species. PMMA host polymer has the ability to retain the liquid part of the electrolytes within the chain segments of the backbone and is much preferred for developing GPEs [3-4].

Although, there are a few reports available in the literature on PMMA based GPEs intended for SIBs [4-7], there are no reports available especially on Raman spectroscopic studies of PMMA based, sodium-ion conducting GPEs formed with NaPF₆ as the ionic salt, EC and PC as the plasticizer and

the solvent, respectively. In this work, electrical and optical properties of PMMA:NaPF₆:EC:PC GPEs have been studied by using Electrochemical Impedance Spectroscopic (EIS) and Raman Spectroscopic techniques to find out the composition with optimized ambient temperature ionic conductivity. The best conducting GPE shows reasonably good ambient temperature ionic conductivity suitable for practical applications.

Materials and Methods

Six different GPEs have been synthesized as the compositions are listed in Table 1 with PMMA (Alfa Aesar) as the host polymer, NaPF₆ (Fluoro Chem Ltd., high purity) as the ionic salt, EC (Ethylene Carbonate) (Sigma-Aldrich) and PC (Propylene Carbonate) (Sigma-Aldrich) as the plasticizer and the solvent, respectively. For the synthesis of GPEs, the ionic salt, EC and PC were magnetically stirred at room temperature for 2 hours, then the PMMA was added and stirred again for 6 hours at 75 °C until a clear homogeneous gel sample was obtained.

Metrohm Autolab (PGSTAT 128N) impedance analyzer in the frequency range from 1 Hz to 0.1 MHz was used for impedance measurements. The temperature of the samples was varied from 20 to 80 °C and the impedance data were recorded at 10 °C intervals on heating. The ionic conductivity for each samples were estimated by finding the bulk resistances in the respective Nyquist plots. Raman spectra for all the GPEs as well as for the raw materials were recorded by using RAM II FT-Raman module connected to a Bruker Vertex 70 FTIR spectrometer with a laser wavelength of 1064 nm. Each recorded spectrum is the average of 500 scans with an optical resolution of 2 cm⁻¹.

Table 1: Sample compositions for six different PMMA based GPEs synthesized in this work.

Sample Number	PMMA (wt%)	NaPF ₆ (wt%)	EC (wt%)	PC (wt%)
1	09	09	41	41
2	10	10	40	40
3	11	11	39	39
4	12	12	38	38
5	13	13	37	37
6	14	14	36	36

Results and Discussion

Fig.1 shows the variation of ionic conductivity with inverse temperature for all the six different compositions of GPEs investigated in this work. These ionic conductivity values were extracted from the impedance data recorded by using the Metrohm Autolab 128N Potentiostat/Galvanostat. Increase in ionic conductivity with temperature is believed to be due to the expansion of the polymer matrix leading to increase in free-volume. The increased free-volume in turn promotes the mobility of the polymer segments and ionic species, resulting in higher ionic conductivity. Ionic conductivity drops to lower values from sample 1 to 6 with the increase of polymer and the salt content. This drop can clearly be seen in Fig.1 for the conductivity values at ambient temperature and is associated with the formation of ion-pairs and aggregates which lead to reduced mobility of ionic species. As listed in Table 2, when we go from sample 1 to 6, ambient temperature ionic conductivity decreases and at the same time the activation energy (E_a) keeps on increasing slightly. Variation of ionic conductivity with inverse temperature follows Arrhenius behavior ($\sigma = \sigma_0 e^{-E_a/kT}$, where σ_0 is the pre-exponential factor) for all six different compositions. The activation energy for each samples were estimated from the slopes of the respective log σ vs inverse temperature plots as illustrated in Fig.2 for Sample #1; the best conducting one. It can be noted that the activation energies for all the sample compositions remain almost constant and the best conducting composition shows an activation energy of 0.14 eV. Optimized composition (sample 1) shows an ionic conductivity value of 4.2 mS cm⁻¹ at ambient temperature (see Table 2). Arrhenius behavior of conductivity variation was already reported by Hashmi *et al.*[8] for a similar PEO based sodium-ion conducting GPE system. Hopping of Na⁺ ionic

species between the coordinating sites and the reduction of anion mobility contribute to the optimized ionic conductivity in 9PMMA:9NaPF₆:41EC:41PC (wt%) GPE. As earlier reported by Yang *et al.*[9] for some other sodium-ion conducting GPE systems, entrapment of liquid electrolyte within the pores of the polymer host and eventual swelling of the amorphous phase content would also contribute to enhance the ionic conductivity.

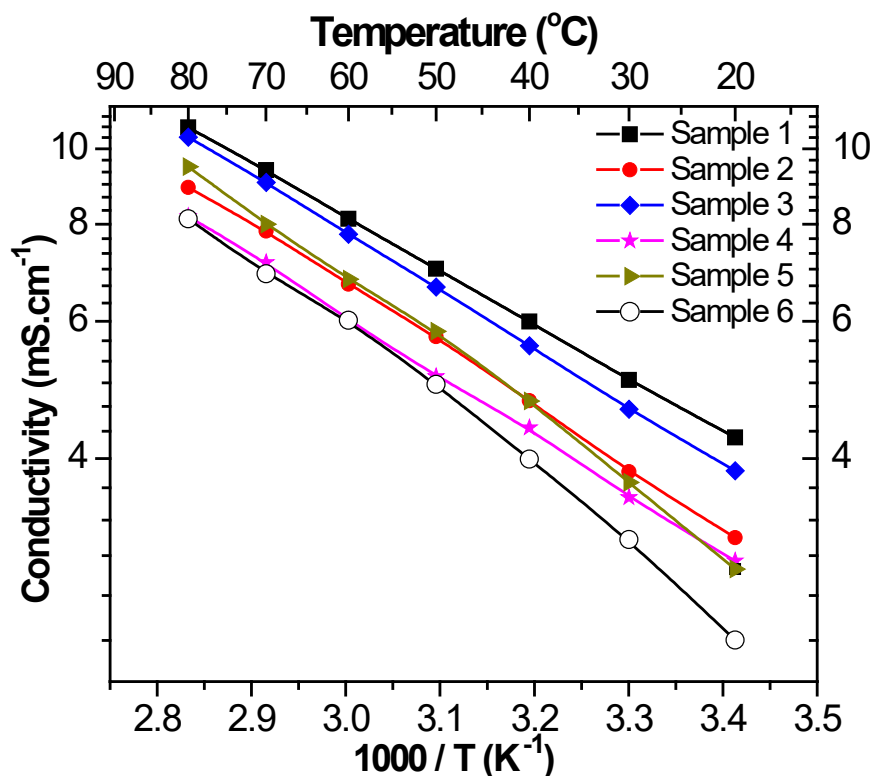


Figure 1: Conductivity variation with inverse temperature for PMMA based GPEs in the temperature range from 20 to 80 °C.

Table 2: Conductivity at 20 °C and the activation energy (E_a) for each of the GPE samples investigated in this work.

Sample Number	σ at 20 °C (mS cm ⁻¹)	E_a (eV)
1	4.2	0.14
2	3.2	0.16
3	3.9	0.15
4	3.0	0.15
5	2.9	0.17
6	2.3	0.18

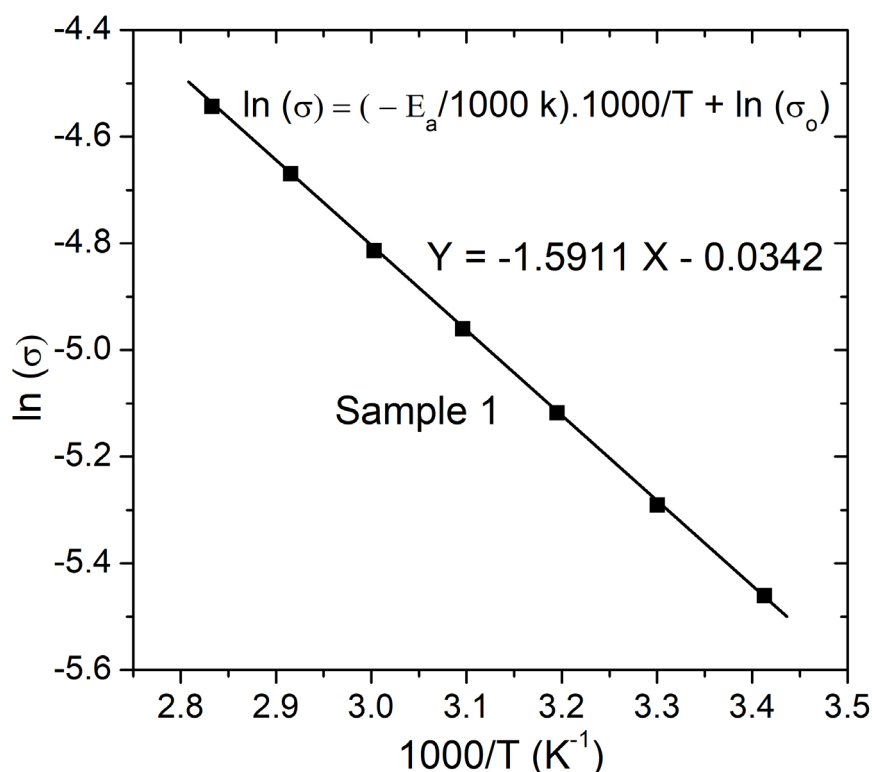


Figure 2: $\ln(\sigma)$ vs inverse temperature plot for best conducting sample (#1) in the temperature range from 20 to 80 °C.

Activation energy is a combination of energy of the defect formation and the energy of defect migration within the polymer chains. As listed in Table 2, E_a remains almost constant showing only an insignificant variation in the second decimal point for different compositions. Hence, the change in conductivity with composition is primarily due to the degree of ionic dissociation, which mainly depends on the concentration of EC, PC and the ionic salt. Our attempts to prepare samples with PMMA wt % less than 9 and higher than 14 were not successful, because of the difficulties in gel formation. We strongly believe that the optimized conductivity of Sample #1 is due to the highest degree of ionic dissociation and increased mobility of ions caused by the higher weight percentages of EC and PC (41 wt% each). PC acts as the solvent and the liquid plasticizer in the GPEs, whereas the EC is mainly a plasticizing agent. It could be noted that the excessive amount of PC will improve ionic conductivity, but will reduce the viscosity leading to hindrance in gel formation. On the other hand, moderate or lower amount of PC will lead to segregation within the gel. It is strongly believed that the optimized composition forms better conducting pathways and optimized ionic dissociation leading to highest conductivity value.

Fig.3 shows the Raman spectra for all the six GPE compositions as well as for the raw materials. As expected, very sharp crystalline peaks (400-850 cm^{-1} wave number range) of NaPF_6 disappear in the gel state of the electrolytes and the Boson modes (less than 200 cm^{-1}) remain almost constant in intensity for all the six different compositions. Boson mode is not present in the NaPF_6 raw material due to the pure crystalline nature of NaPF_6 . A very strong Raman band at 2928 cm^{-1} , which appears in all the GPE compositions as well as in PMMA, EC and PC is due to the C-H asymmetric stretching vibration of the methylene (CH_2) group. Another set of strong Raman bands at 650-950 cm^{-1} , which appears in all the six GPEs as well as in EC could be associated with the C-O in-plane bending (720 cm^{-1}) and CH_3 rocking (895 cm^{-1}) vibrations arising from EC [10].

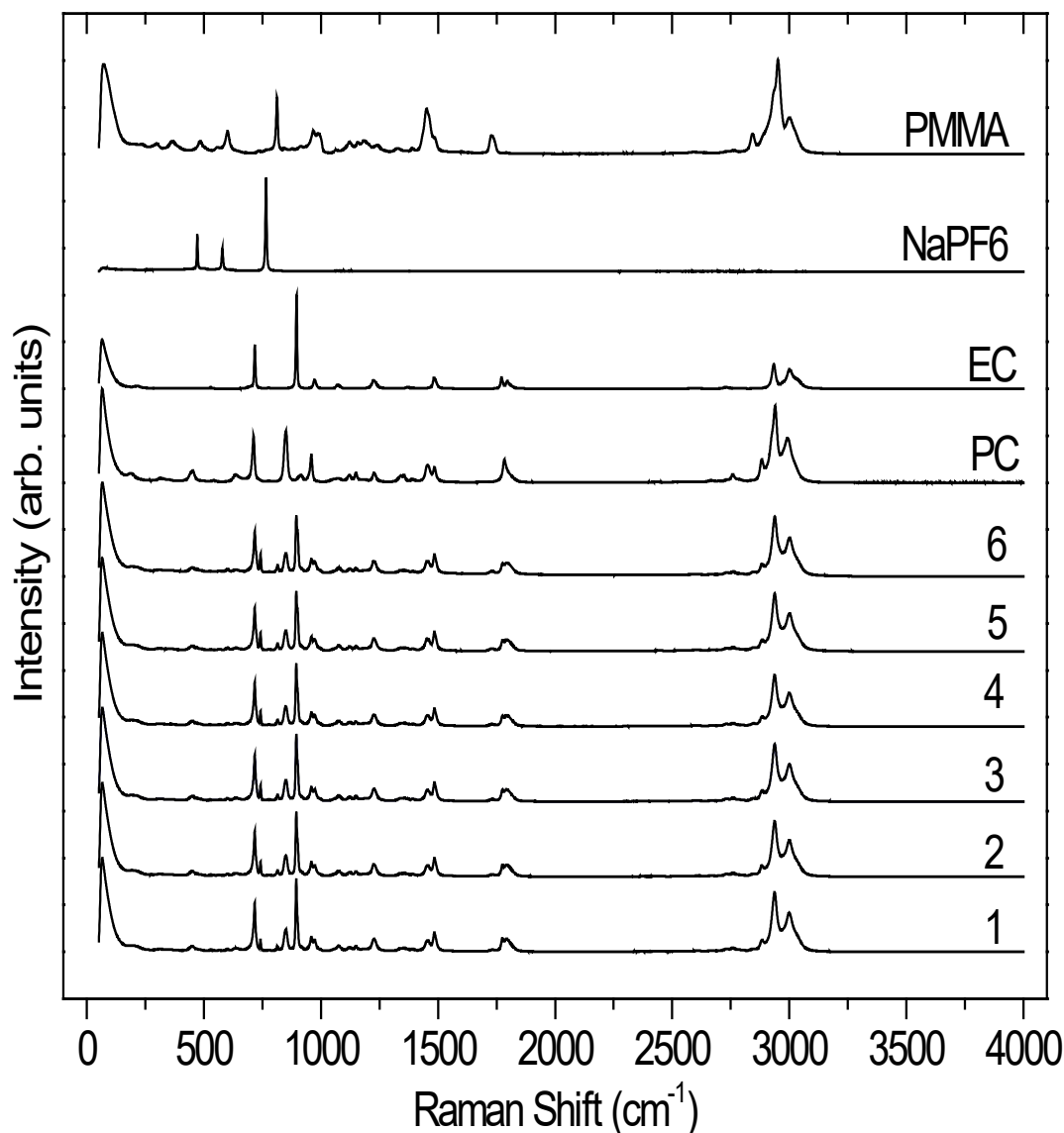


Figure 3: Raman shift in the wave number range 0 - 4000 cm^{-1} for six different compositions of PMMA based GPEs and for the raw materials; PMMA, NaPF₆, EC and PC.

Conclusion

Six different compositions of PMMA based sodium-ion conducting GPEs have been synthesized and characterized. The GPE 9PMMA:9NaPF₆:41EC:41PC (wt%) showed the best ambient temperature ionic conductivity of 4.2 mS cm^{-1} . Variation of ionic conductivity with inverse temperature showed Arrhenius behavior with almost constant activation energies. The best conducting GPE showed an activation energy of 0.14 eV. In the Raman spectra, very sharp crystalline peaks (400-850 cm^{-1} wave number range) of NaPF₆ disappear in the gel state of the electrolytes confirming the non-crystalline nature of the GPEs. Boson modes remain almost constant in intensity for all the six different compositions. The best conducting GPE seems to be highly suitable for practical applications in SIBs.

Acknowledgement

This research was supported by the Accelerating Higher Education Expansion and Development (AHEAD) Operation of the Ministry of Higher Education, Sri Lanka funded by the World Bank (DOR Project # 62) and The World Academy of Sciences (TWAS), Trieste, Italy (Grant #:17-354 RG/PHYS/AS-I-FR3240297743).

References

- [1] S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh and K. Fujiwara, Electrochemical Na insertion and solid electrolyte interphase for hard-carbon electrodes and application to Na-ion batteries, *Advanced Functional Materials* 21(20) (2011) 3859-3867
- [2] K. Vignarooban, R. Kushagra, A. Elango, P. Badami, B.-E. Mellander, X. Xu, T.G. Tucker, C. Nam and A.M. Kannan, Current trends and future challenges of electrolytes for sodium-ion batteries, *International Journal of Hydrogen Energy* 41 (2016) 2829-2846
- [3] J. Shi, H. Xiong, Y. Yang and H. Shao, Nano-sized oxide filled composite PEO/PMMA/PVdF-HFP gel-polymer electrolyte for rechargeable lithium and sodium batteries, *Solid State Ionics* 326 (2018) 136-144
- [4] D. Kumar and S.A. Hashmi, Ion transport and ion-filler-polymer interaction in poly (methyl methacrylate) based, sodium-ion conducting, gel-polymer electrolytes dispersed with silica nanoparticles, *Journal of Power Sources* 195 (2010) 5101-5108
- [5] K. Mishra, T. Arif, R. Kumar and D. Kumar, Effect of Al₂O₃ nanoparticles on ionic conductivity of PVdF-HFP/PMMA blend-based Na⁺ ion conducting nanocomposite gel-polymer electrolyte, *Journal of Solid State Electrochemistry* 23 (2019) 2401-2409
- [6] Y. Xue and D.J. Quesnel, Synthesis and electrochemical study of sodium-ion transport polymer gel electrolytes, *RSC Advances* 6 (2016) 7504-7510
- [7] J. Vondrak, M. Sedlarikova, J. Velicka, B. Klapste, V. Novak and J. Reiter, Gel-polymer electrolytes based on PMMA, *Electrochimica Acta* 46 (2001) 2047-2048
- [8] S.A. Hashmi and S. Chandra, Experimental investigations on a sodium-ion conducting polymer electrolyte based on poly (ethylene oxide) complexed with NaPF₆, *Materials Science and Engineering B* 34 (1995) 18-26
- [9] Y.Q. Yang, Z. Chang, M.X. Li, X.W. Wang and Y.P. Wu, A sodium-ion conducting gel-polymer electrolyte, *Solid State Ionics* 269 (2015) 1-7
- [10] M.R.H. Mas Haris, S. Kathiresan and S. Mohan, FTIR and FT-Raman spectra and normal co-ordinate analysis of poly (methyl methacrylate), *Der Pharma Chemica* 2(4) (2010) 316-323