



Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Short communication

Electric field induced enhancement in the interfacial charge transfer kinetics of a solid polymer electrolyte

K. Ragavendran, D. Vasudevan*, Bosco Emmanuel

Central Electrochemical Research Institute, Karaikudi 630006, Tamilnadu, India

ARTICLE INFO

Article history:

Received 29 May 2008

Received in revised form

23 September 2008

Accepted 9 October 2008

Keywords:

Solid polymer electrolyte

AC impedance

Interfacial charge transfer resistance

KYNAR

Electrets

Lithium batteries

ABSTRACT

A novel electrostatic method for preparing modified solid polymer electrolytes (SPEs) is reported. Application of an electric field on an evaporating mixture of KYNAR, ethylene carbonate (EC), propylene carbonate (PC) and LiPF₆ dissolved in tetra hydro furan (THF) resulted in a solid polymer electrolyte whose charge transfer resistance was at least an order of magnitude lower than that formed without the application of an electric field. We believe that the observed enhancement is probably due to an electric field induced orientation of dipoles in the polymer chain.

© 2008 Elsevier B.V. All rights reserved.

Solid polymer electrolytes (SPEs) have attracted considerable scientific and technological attention because of their interesting physics and applications such as in electrochemical devices, electro-organic synthesis, etc. [1–4]. The great advantage in using an SPE in energy devices such as the lithium batteries is safety compared to the use of conventional liquid electrolytes [5]. However, low ionic conductivity and high charge transfer resistance at polymer electrolyte/electrode interfaces are the drawbacks.

Despite many studies about improvements in the ionic conductivity [6,7], only a few investigations have focused on improving the charge transfer kinetics at the interfaces. The use of polymer electrolytes with better charge transfer kinetics is mandatory to obtain improvements in the charge/discharge capability of a lithium battery, improved kinetic efficiency of fuel cells, superior response time in electrochemical sensors and low cell voltages in electro-organic synthesis and hence reduced scaling up costs.

This short communication reports the results of our preliminary investigations on an electric field induced improvements in the interfacial charge transfer kinetics of a fluorine based polymer electrolyte. It is pertinent to mention here that fluorine based polymers are well known for their strong piezo electric properties [8].

Orientation of the polymer chain is a major factor that dictates the ionics of soft condensed matter (a polymer electrolyte for exam-

ple). Application of an electric field on a suitable dielectric material (in the fluid state) causes the repositioning of the charge carriers or alignment of the dipoles within the material which gets frozen in position upon solidification. Such materials are known as electrets [9] and the term was coined by Oliver Heaviside in the year 1885. This gave us the idea that the application of an electric field on a solidifying polymer electrolyte could improve the performance of an SPE through the formation of electrets. It is also known in the literature that fluoro polymers are known to form electrets upon the application of an electric field [10]. Hence, we chose KYNAR (a copolymer made of poly vinylidene fluoride and hexa fluoro propylene) complexed with LiPF₆ for our studies.

As we shall show below, application of an electric field on an evaporating mixture of KYNAR, ethylene carbonate (EC), propylene carbonate (PC) and LiPF₆ dissolved in tetra hydro furan (THF) resulted in a solid polymer electrolyte whose charge transfer resistance was at least an order of magnitude lower than that formed without the application of an electric field. We believe that the observed enhancement is probably due to an electric field induced orientation of dipoles in the polymer chain.

KYNAR, lithium hexa fluoro phosphate (LiPF₆), EC and PC (all of AR grade) in the ratio (w/w) 3:1:3:3 were dissolved in THF solvent. The solution formed thus was poured over an inert plastic sheet and allowed to evaporate at room temperature (sample A). Another sample was formed by applying an electric field (30 V) to the evaporating solution of the polymer mixture (sample B). The electric field was applied to the evaporating solution of the electrolyte which

* Corresponding author.

E-mail address: vasudevand@rediffmail.com (D. Vasudevan).

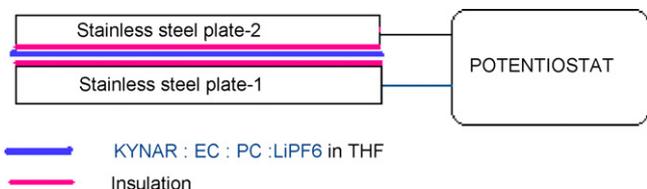


Fig. 1. Experimental setup for sample B preparation. Sample A was prepared using the same setup but with zero field (sample C was prepared under zero field conditions with the insulation removed and sample D was prepared under an impressed electric field with the insulation removed).

was kept in between the two insulated stainless steel plates connected to a potentiostat which provided the voltage required to generate the electric field. Fig. 1 shows the experimental setup for preparing sample B. Complex plane impedance analysis on samples A and B were carried out using an EIS-Princeton Applied Research-AC-impedance analyzer in the frequency range 100 kHz to 10 mHz with an AC amplitude of 10 mV.

Fig. 2a and b show the complex plane impedance spectra of samples A and B, respectively. The impedance plots were fitted to a Voigt element (a capacitor and a resistor in parallel) as shown

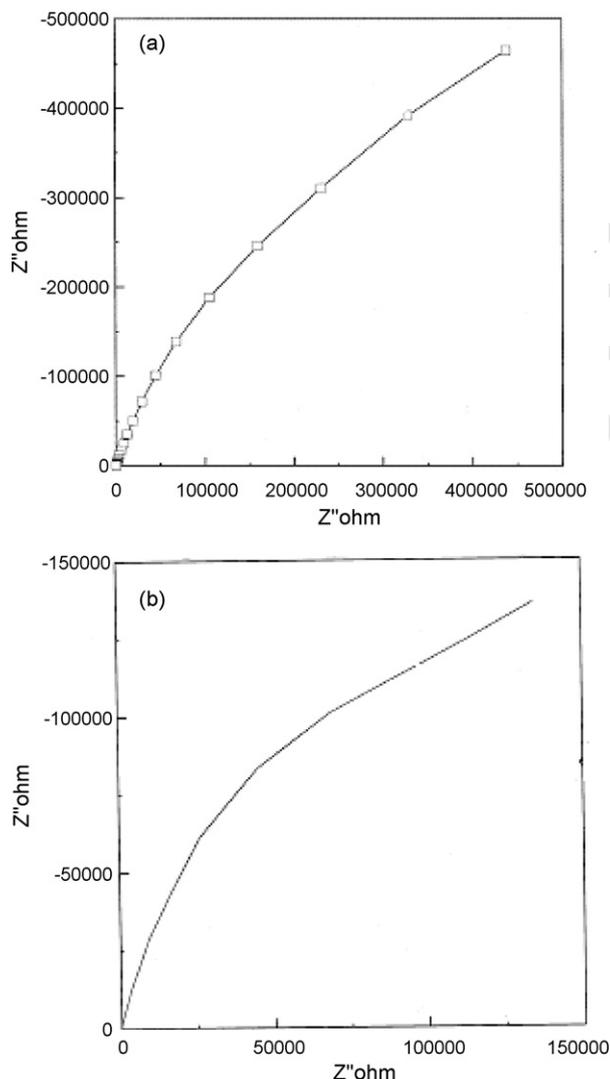


Fig. 2. (a) Complex plane impedance plot of sample A (polymer electrolyte prepared under zero field conditions). (b) Complex plane impedance plot of sample B (polymer electrolyte prepared under an impressed field condition).

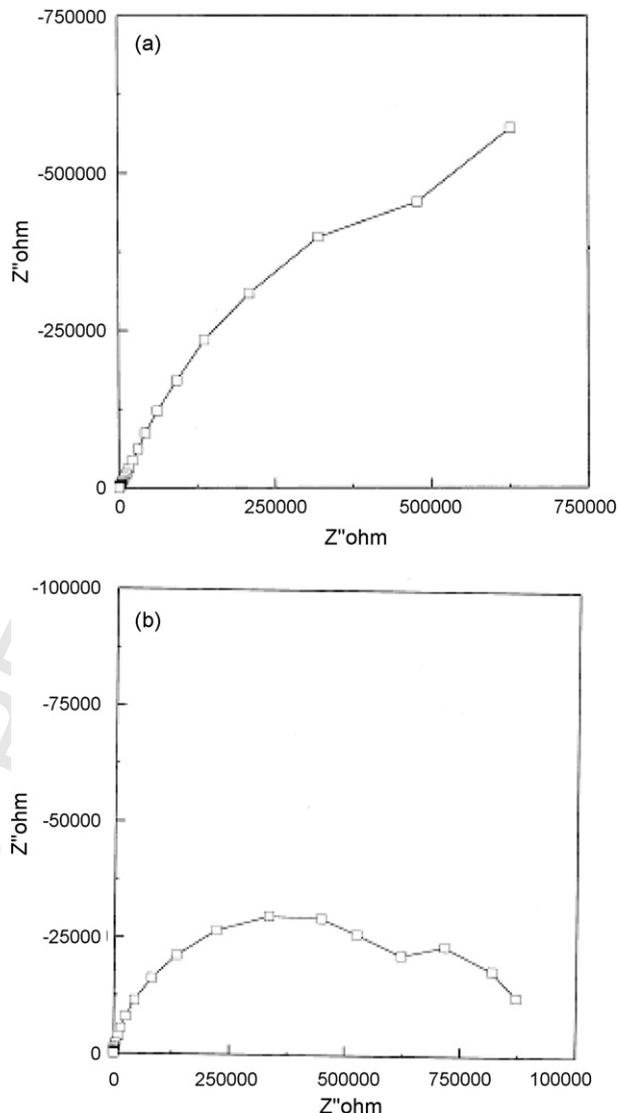


Fig. 3. (a) Complex plane impedance plot of sample C (polymer electrolyte prepared under zero field condition and without an insulation over the stainless steel plates). (b) Complex plane impedance plot of sample D (polymer electrolyte prepared under an impressed field condition and without the insulation over the stainless steel plates).

in Fig. 3. According to the theory of AC-impedance, as applied to metal-electrolyte interfaces the diameter of the semicircle in the Nyquist plot corresponds to the interfacial charge transfer resistance (R_{CT}) and not to any bulk property. Thus, the diameter of the semicircle gives the interfacial charge transfer resistance (R_{CT}) and the capacitance values may be obtained from the maximum in the Nyquist plot (Table 1). It is evident from Table 1 that the application of an electric field improves the R_{CT} value of the SPE by around one order of magnitude. However, it is interesting to note that there

Table 1
 R_{CT} and capacitance values of samples A-D.

| Sample | R_{CT}^* (Ohms) | | Capacitance* (Farads) | |
|----------|---------------------|---------------------|-------------------------|------------------------|
| | Semicircle-1 | Semicircle-2 | Semicircle-1 | Semicircle-2 |
| Sample A | 1.55×10^6 | - | 3.80×10^{-6} | - |
| Sample B | 2.82×10^5 | - | 3.50×10^{-6} | - |
| Sample C | 1.708×10^6 | - | 2.1597×10^{-6} | - |
| Sample D | 7.52×10^4 | 3.768×10^4 | 6.113×10^{-6} | 6.027×10^{-5} |

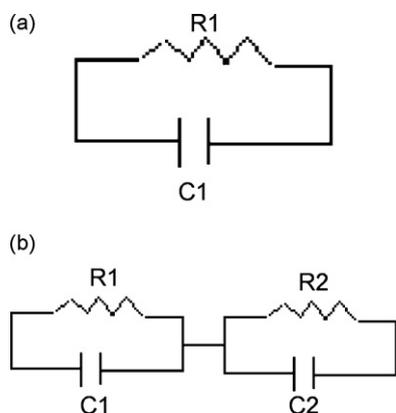


Fig. 4. (a) Voigt element (RC parallel circuit) used to represent the impedance plots given in Figs. 2a, b and 3a. (b) Two Voigt elements (RC parallel circuits, in series) used to represent the impedance plots given in Fig. 3b.

is no significant change in capacitance due to the impressed field (Fig. 4)

We also investigated two more polymer electrolyte films (samples C and D) whose compositions and the method of preparation were exactly the same as that adopted for samples A and B. The only difference was that, in the preparation of the present samples (C and D) there was no insulation over the stainless steel plates. The evaporating polymer electrolyte mixture was poured over the stainless steel plate 1 which was thoroughly washed with acetone. Our motivation was to apply an electric field (and not to pass an electric current) through the evaporating electrolyte mixture and hence care was taken that the electrolyte touched the plate 1 but not the plate 2. The distance of separation between the electrolyte mixture and the plate 2 was ~ 2 mm. In the presence of the 2 mm gap, a DC current cannot be sustained by applying a potential difference between the plates. However, an electrical field can be sustained. We believe that it is this electrical field which is aligning the polymer chains.

Fig. 3a and b respectively show the complex plane impedance spectra of the polymer films prepared under zero field (sample C) and with field (sample D) condition. Fig. 3a was fitted to a single Voigt element and Fig. 3b was fitted to two Voigt elements connected in series. The charge transfer resistance (R_{CT}) and capacitance values for these samples (C and D) are given in Table 1. It is interesting to note that while the R_{CT} value has decreased by two orders of magnitude for the with field case, the capacitance value is almost the same as that for the zero field case.

The multiple semi circles observed in Fig. 3b indicate two interfacial processes occurring simultaneously. The identity of these two interfacial processes is yet to be established. One possible reason for the emergence of an additional semicircle may be that the bare (no insulation) steel plate might have provided the electrolyte with some impurities which might have got doped into the electrolyte. This doping mechanism, which is yet to be confirmed, combined with the polymer chain alignment mechanism might be responsible for the observed two orders of magnitude decrease in R_{CT} , compared to that in Fig. 2b where the magnitude of decrease in R_{CT} is one order.

Though electrets are well known in literature, this is the first time that the idea has been exploited to prepare modified SPEs for application in lithium batteries. We believe that our finding will benefit both the power sources community and polymer physicists by opening up a new avenue in polymer electrolyte research. At present, we are looking at the physics and electrochemical applications of this electro statically modified SPE. Detailed work along these lines are at progress in our laboratory and the results will be shortly communicated as an extensive paper elsewhere.

Acknowledgements

This work was partly supported by the Department of Science and Technology (Govt. of India, New Delhi) through a project GAP 39/05 on lithium batteries. One of the authors K.R. thanks the CSIR, Govt. of India for the award of an Extended Senior Research Fellowship. The authors thank Dr. Venkatachari and Dr. Muralidharan for extending their AC-impedance facility.

References

- [1] J.-M. Tarascon, M. Armand, *Nature* 414 (2001) 359.
- [2] Y. Kimura, M. Asano, J. Chen, Y. Maekawa, R. Katakai, M. Yoshida, *Radiation Physics and Chemistry* 77 (2008) 864.
- [3] A. Kunugi, M. Fujioka, M. Yasuzawa, M. Inaba, Z. Ogumi, *Electrochimica Acta* 44 (1998) 653.
- [4] X. Lu, S. Wu, L. Wang, Z. Su, *Sensors and Actuators B: Chemical* 107 (2005) 812.
- [5] F.M. Gray, *Polymer Electrolytes*, RSC Monographs, The Royal Society of Chemistry, London, 1997.
- [6] A.M. Christie, S.J. Lille, E. Staunton, Y.G. Andreev, P.G. Bruce, *Nature* 433 (2005) 50.
- [7] T.J. Singh, G. Sanjeev, K. Siddappa, S.V. Bhat, *Journal of Polymer Science Part B: Polymer Physics* 42 (2004) 1299.
- [8] H. Kawai, *Japanese Journal of Applied Physics* 8 (1969) 975.
- [9] R.P. Feynman, R.B. Leighton, M. Sands, *The Feynman Lectures on Physics*, vol. 2, Addison-Wesley/Narosa, New Delhi, 1986, pp. 8-11.
- [10] Jefimenko, D. Oleg, K. David, Walker, *Journal of Applied Physics* 44 (1973) 3459.