

Impedance Analysis of Heat Treated Polyethylene Oxide Polymeric Material for a Neural Storage Application

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Abstract: Problem statement: From the early days of, researchers have developed electronic models of neurons designed to emulate neural behavior with electrical signals that mimic in some ways the measured potentials of biological neurons. Researchers interested in fabricating artificial neurons have long sought a simple and techniques to produce devices that efficiently store synaptic weights, which is behind holding a particular state in relation to conductance parameters. As Engineers become closer to realizing accurate hardware models of neurons, the need for a simple analog memory device grows correspondingly. To determine the storage characteristics of polyethylene oxide based polymer as the base material for high charge storage analogue neural switch. **Approach:** Various devices prepared under controlled conditions. Each device tested for its impedance characteristics as a function of both frequency and temperature. Mathematical model developed to account for the obtained characteristics. **Results:** The heat treated devices showed stability, repeatability and ability to store enough charge for long time periods. Impedance analysis proved a similar response to the actual neural switches. **Conclusion:** The symmetrical behavior for such devices opened a wide application area for the manufacturing of low and high frequency analogue devices for intelligent system applications.

Key words: Neural, modeling, memory, information processing, polymers, storage

INTRODUCTION

The design of an artificial neural device can help in future implementations and studies in the fields of memories, neural networks, intelligent computers and medical applications to name a few. The design and implementation provides a good insight into the process of combining high charge storage materials to produce intelligent switching elements. Such devices may be used to control and modulate the communication between different artificial neurons.

Solid polymer electrolyte systems have been widely used as potential technological applications in energy and charge storage. It is apparent that these materials show ionic conductivity when ionic salts are dissolved in them. The mechanism of ionic mobility is still controversial.

Amorphous polyethylene oxide based materials doped with alkali-metal salts are favored candidates for use as electrolytes in solid-state rechargeable storage medium. Among others, a highly attractive avenue to achieving both high ionic conductivity and dimensional stability consists in covalently bonding an amorphous low glass transition temperature PEO-based polymer to a second polymer, thereby forming a block copolymer. Such a copolymer will either be segmentally mixed disordered or microphase separated ordered into

periodically spaced nanoscale domains of the different blocks, with the covalent junction residing at the interface.

Polymers carrying electronegative atoms oxygen or nitrogen in their repeat unit can act as solvents for certain salts, as a consequence of the attractive interaction between cations and the polymer. A prototype class of such polymer electrolytes are polyethers, e.g., polyethyleneoxide (PEO), complexed with Li salts that contain a highly polarizable anion. These materials can show significant ionic conductivities offering applications as electrolyte material in rechargeable lithium-polymer storage media^[1-5].

Background: Ethylene oxide (CH₂ CH₂O) is highly reactive with particular importance as a chemical intermediate due to the tendency of the ring to open in the presence of ionic catalyst. Co-dissolving an alkali metal salt with PEO [HO(CH₂CH₂O)_nH] and removal of the solvent will result in a mixed phase system which retains, in part, a complex of the polymer and the salt. It is shown that the paired ether oxygen electrons, which give the polymer strong hydrogen - bonding affinity, can also be involved in association reactions with a variety of monomeric and polymeric electron acceptors with polymer-alkali salts recognized as fast ionic

conductors with wide charge storage using them as solid electrolytes in batteries, chemical sensors and other applications e applications^[6-12]. For pure PEO the crystalline phase occupies approximately 80% of the available volume, with the remainder being taken up by a dispersed amorphous phase. On addition of LiCF_3SO_3 , Li^+ ions form cross-links between ethylene oxide segments of neighboring chains as the cation (Li^+) forms ionic bonds with the negatively polarized oxygen atoms forming a closed helical structure with the (Li^+) ions inside. The CF_3SO_3^- anion forms another ionic bond with the methylene group outside the helical structure when the ring structured monomers. It is suggested that ionic conduction in $\text{PEO}_x\text{LiCF}_3\text{SO}_3$ occurs by the cation (Li^+) hopping between sites in either the single or double helix structures. However, this hopping model was discredited other by studies, which showed the ionic conductivity occurred mainly in the amorphous phase rather than in the crystalline phase. Furthermore experiments with dopant ions that form immobile ion pairs indicated that transport was not occurring down a helical path. A variety of experiments showed that ion transport in the majority of the polymer-salt complexes occurs through segmental motion of the polymer^[13-15].

MATERIALS AND METHODS

Polymer films were prepared using poly (ethylene oxide) with average molecular weight of 5×10^6 Daltons (Da) and density of 1.21 at 65°C and lithium trifluoromethane sulfonate 97% pure. The required amounts of lithium salt and polyethylene oxide (PEO), to give an O: Li ratio of 10: 1, were dissolved in acetonitrile 99% pure under nitrogen atmosphere. The solution was then stirred at room temperature for 48 hours after which the solution was filtered to remove any un-dissolved materials and stored in 14, 2 mL plastic containers and kept well isolated from the atmosphere.

The polymeric films were deposited using a drop coating technique and then dried by heating for 30 and in an oven at 50°C .

RESULTS

Figure 1 shows the complex impedance of a heat treated device as a function of frequency.

Both real and imaginary parts of the complex impedance behave in a symmetrical but opposite manner as a logarithmic function of frequency, where at any value within a range of frequencies the product of the real and imaginary parts is negative. As the real part is positive and decreasing with frequency while the imaginary part is negative and increasing with frequency,

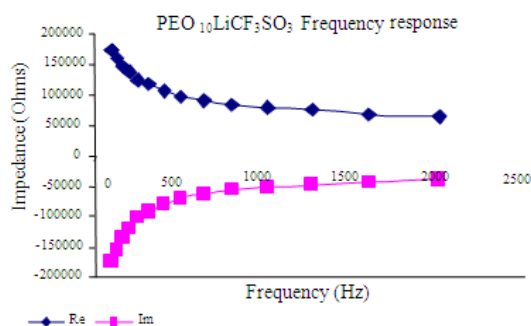


Fig. 1: Device frequency response

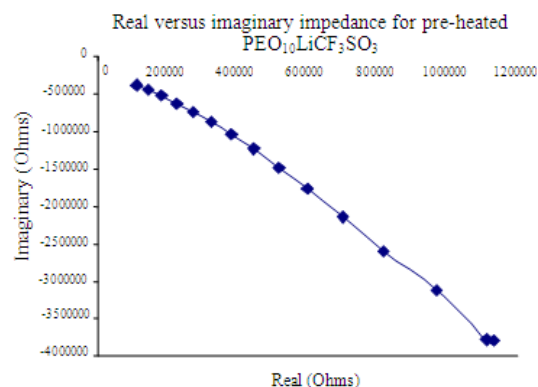


Fig. 2: Relationship between real and imaginary impedances

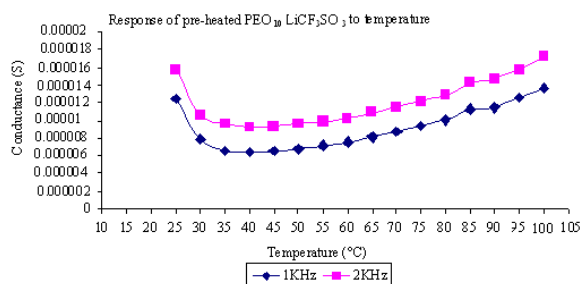


Fig. 3: Conductance characteristics

then a model which readily presents itself is a parallel combination of a resistor and capacitor with no evidence of a double layer capacitance as the plots representing the real versus the imaginary parts, as shown in Fig. 2, do not show a spur at low frequencies, with Fig. 3 showing an important Frequency-Temperature characteristics.

DISCUSSION

Complex impedance characterization was carried out to determine the device response.

The real and imaginary parts of the complex impedance function can be obtained as follows:

$$Y = G + j\omega c = \left[\frac{1 + j\omega cR}{R} \right] \quad (1)$$

So:

$$Z = \left(\frac{R}{1 + j\omega cR} \right) = \left[\frac{R(1 - j\omega cR)}{(1 + j\omega cR)(1 - j\omega cR)} \right] = \left[\frac{R - j\omega cR^2}{1 + \omega^2 c^2 R^2} \right] \quad (2)$$

$$\text{Re}(Z) = \left[\frac{R}{1 + \omega^2 c^2 R^2} \right] \quad (3)$$

$$\text{Im}(Z) = - \left[\frac{\omega c R^2}{1 + \omega^2 c^2 R^2} \right] \quad (4)$$

So.

However, when the complex impedance characteristics are closely examined, it is found that a logarithmic function is involved as follows:

$$\text{Re}(Z) = \left(\frac{R}{1 + \omega^2 c^2 R^2} \right) \log \left(\frac{2\omega_c}{\omega} \right) \quad (5)$$

$$\text{Im}(Z) = \left(\frac{\omega c R^2}{1 + \omega^2 c^2 R^2} \right) \log \left(\frac{\omega}{\omega_c} \right) \quad (6)$$

where, ω_c is the crossing frequency of the zero frequency axis. Further analysis showed that both real and imaginary parts would intersect at angular frequency ω_i given by:

$$\omega_i = \left(\frac{3}{2} \omega_c \right) \quad (7)$$

Figure 2 shows an evidence supporting the claim of almost total phase conversion (as the device is heated up to 100°C and then cooled rapidly before being tested). An amorphous phase observed to be retained in the tested devices with a downward concavity and no inflection points indicating a homogeneous phase as temperature changes. This further suggests a stable formation of amorphous phase occupying the majority of the material volume as the device is heat treated.

Figure 3 shows device conductance response as a function of temperature at two different frequencies. The plots illustrate the effect of temperature on increasing the conductivity of the device, which is expected as the rate of cation-anion recombination

increases. The plots also show a comparable conductance for low and high ends, which enable operating the device at low temperatures and also indicate stability at very high temperatures as the conductance returns to a value close to the one at low temperature. Effect of increasing operational frequency within a limited low range is also observed, as conductance increases at higher frequencies due to faster cation-anion recombination rates^[16-21].

CONCLUSION

Analysis of the device characteristics showed a non-Arrhenius temperature dependence of the device conductance which indicates that the conductivity behavior of PEO₁₀LiCF₃SO₃ is governed by much more complicated form of dynamics with obvious dependency of both the real and imaginary parts on frequency. The impedance characteristics were very encouraging in terms of neural storage application, which uses analogue logic activation signals and respond to temperature and frequency in a symmetrical manner.

REFERENCES

1. Duan, Y. and J.W. Halley, 2005. Mechanisms of lithium transport in amorphous polyethylene oxide. *J. Chem. Phys.*, 122: 054702. DOI: 10.1063/1.1839555
2. Pradhan, D.K., R.N.P. Choudhary, B.K. Samantaray, N.K. Karan and R.S. Katiyar, 2007. Effect of plasticizer on structural and electrical properties of polymer nanocomposite electrolytes. *Int. J. Electrochem. Sci.*, 2: 861-871. <http://electrochemsci.org/list07.htm#issue11>
3. Shukla, A.K. and T.P. Kumar, 2008. Materials for next-generation lithium batter. *Curr. Sci.*, 94: 314-331. <http://www.ias.ac.in/currsci/feb102008/314.pdf>
4. Krishnan, M. and S. Balasubramanian, 2004. Order-disorder transitions and melting in a helical polymer crystal: Molecular dynamics calculations of model poly (ethylene oxide). *Chem. Phys. Lett.*, 385: 351-356. <http://cat.inist.fr/?aModele=afficheN&cpsidt=15500487>
5. Grujicic, M. *et al.*, 2005. An atomic level analysis of conductivity and strength in poly (ethylene oxide) sulfonic acid-based solid polymer electrolytes. *Mater. Sci. Eng. B-Solid State Mater. Adv. Tech.*, 117: 187-197. <http://cat.inist.fr/?aModele=afficheN&cpsidt=16556428>

6. Ho, D.L., B. Hammouda, S.R. Kline and W.R. Chen, 2005. Unusual phase behavior in mixtures of poly (ethyleneoxide) and ethyl alcohol. *J. Polymer Sci. Part B. Polymer Phys.*, 15: 557-564. DOI: 10.1002/polb.20726
7. Judeinstein, P., D. Reichert, E.R. deAzevedo and T.J. Bonagambace, 2005. NMR multi-scale description of ionic conductivity mechanisms inside polymer electrolytes. *Acta Chimica Slovenica*, 52: 349-360. <http://acta.chem-soc.si/52/52-4-349.pdf>
8. Yu, H., V. Gunsteren and F. Wilfred, 2005. Accounting for polarization in molecular simulation. *Comput. Phys. Commun.*, 172: 69-85. DOI: 10.1016/j.cpc.2005.01.022
9. Tao, Z. and P.T. Cummings, 2007. Molecular dynamics simulation of inorganic ions in PEOaqueous solution. *Mol. Simulat.*, 33: 1255-1260. DOI: 10.1080/08927020701697691
10. Blazejczyk, A., W. Wieczorek, R. Kovarsky, D. Golodnitsky, E. Peled, L.G. Scanlon, G.B. Appetecchi and B. Scrosatid, 2004. Novel solid polymer electrolytes with single lithium-ion transport. *J. Electrochem. Soc.*, 151: A1762-A1766. DOI: 10.1149/1.1793714
11. Hehmeyer, O.J., G. Arya and A.Z. Panagiotopoulos, 2007. Monte carlo simulation and molecular theory of tethered polyelectrolytes. *J. Chem. Phys.*, 126: 1-11. DOI: 10.1063/1.2747600
12. Curtright, A.E., P.J. Bouwman, R.C. Wartena and K.E. Swider-Lyons, 2004. Power sources for nanotechnology. *Int. J. Nanotechnol.*, 1: 226-239. DOI: 10.1504/IJNT.2004.003726
13. Moore, S.W. and P. Schneider, 2001. A review of cell equalization methods for lithium ion and lithium polymer battery systems. http://www.americansolarchallenge.org/tech/resources/SAE_2001-01-0959.pdf
14. Turcu1, R., D. Bica, L. Vekas, N. Aldea1, D. Macovei, A. Nan, O. Pana1, O. Marinica, R. Grecu and C.V.L. Pop, 2006. Synthesis and characterization of nanostructured polypyrrole-magnetic particles hybrid material. *Romanian Rep. Phys.*, 58: 359-367. http://alpha1.infim.ro/rfp/2006_58_3/art15Turcu.pdf
15. Anne-Vale´rie Ruzette, G., P. Philip Soo, R. Donald Sadoway and M. Anne Mayesz, 2001. Melt-formable block copolymer electrolytes for lithium rechargeable batteries. *J. Electrochem. Soc.*, 148: A537-A543. <http://cat.inist.fr/?aModele=afficheN&cpsidt=1049255>
16. Mui, S.C., P.E. Trapa, B. Huang, P.P. Soo and M.I. Lozow *et al.*, 2002. Block copolymer-templated nanocomposite electrodes for rechargeable lithium batteries. *J. Electrochem. Soc.*, 149: A1610-A1615. DOI: 10.1149/1.1518482
17. Song, S., K.D. Miller and L.F. Abbott, 2000. Competitive Hebbian learning through spike-timing dependent synaptic plasticity. *Nature Neurosci.*, 3: 919-926.
18. Bi, G. and M. Poo, 2001. Synaptic modification by correlated activity: Hebb's postulate revisited. *Annu. Rev. Neurosci.*, 24: 139-166. <http://www.citeulike.org/user/mura/article/785613>
19. Latham, P.E., B.J. Richmond, S. Nirenberg and P.G. Nelson, 2000. Intrinsic dynamics in neuronal networks II: Experiment. *J. Neurophysiol.*, 83: 828-835. <http://jn.physiology.org/cgi/content/abstract/83/2/828>
20. Li, C.M., C.Q. Sun, W. Chen and L. Pan, 2005. Electrochemical thin film deposition of polypyrrole on different substrates. *Surface Coat. Technol.*, 198: 474-477. DOI: 10.1016/j.surfcoat.2004.10.065
21. Aray, Y., M. Marquez, J. Rodrı´guez, D. Vega, Y. Simo´n-Manso, S. Coll, C. Gonzalez and D.A. Weitz, 2004. Electrostatics for exploring the nature of the hydrogen bonding in polyethylene oxide hydration. *J. Phys. Chem. B.*, 108: 2418-2424. <http://www.seas.harvard.edu/weitzlab/papers/marquez.jpcb.04.pdfN&cpsidt=16273582>