AC Analysis of PEO$_{10}$LiCF$_3$SO$_3$ Polymeric Material for Memory Storage Application

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Abstract: Problem statement: Intelligent systems that need to accurately represent human brain requires analogue devices such as a neural switch that processes decision signals and can actually remember the made decision. Polymeric material such as PEO$_{10}$LiCF$_3$SO$_3$, which previously used in high energy, long life storage batteries, is used here to implement the principle of storage with the required analogue memory. **Approach:** A number of PEO$_{10}$LiCF$_3$SO$_3$ devices tested in a controlled environment and their impedance response to both frequency and temperature recorded, analyzed and plotted for interpretation. **Results:** The tested devices showed ability for charge storage due to its variable impedance response at a range of frequencies, while sustaining very high impedance at DC. The device response found to be affected by intermediate temperatures, with symmetrical response at both low, mid and high temperatures. **Conclusion:** The designed and tested device showed promising characteristics in terms of memory storage as a neural switch. Its high impedance at DC and low impedance at high frequencies with logarithmic response represented the desired features in a reprogrammable analogue device.

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

INTRODUCTION

Polymer electrolytes, in particular polyethylene oxide-alkali salt complexes and the extensively studied polyethylene oxide-lithium trifluoromethane sulphonate (PEO$_{10}$LiCF$_3$SO$_3$), have been applied as materials for high energy, long life, flexible re-chargeable batteries with good mechanical and stable electrochemical properties (Duan and Halley, 2005; Pradhan *et al*., 2007; Shukla and Kumar, 2008; Krishnan and Balasubramanian, 2004; Grujicic *et al*., 2005). Moreover the remarkable achievement of producing highly conducting polymers, such as Polypyrrole with excellent chemical and thermal stability and its ability to switch between two states, namely conducting (oxidized) and insulating (reduced) has brought about the idea of combining these polymers to produce an ionic-electronic interacting mixed conductor. Such a device should have the ability to store the injected charge, affecting its conduction and switches states due to device resistance change. Conception and industrial production of viable high specific energy-power batteries is an important issue for the development of neural storage elements. In terms of stored energy and safety, solid-state devices using polymer electrolytes are highly desirable. One of the most studied systems is Polyethylene Oxide (PEO) complexed by Li salts.

Polymer segmental motions and ionic conductivity are closely related. Bulk PEO is actually a biphasic system where an amorphous and a crystalline state coexist.

PEO is an interesting system because it is soluble in both water and several organic solvents, due to the presence of both hydrophobic and hydrophilic segments.

Since this polymer is soluble in many different solvents, it is widely used in both industrial and biological applications. Industrial applications of PEO include use as a support for organic synthesis reactions, use as a conductive polymer matrix when mixed with salt and use as a membrane material for the separation of acid gases. In biology, PEO is used to crystallize proteins and is considered biologically inert allowing it to be used in medical applications. PEO is also used as a drug delivery matrix and as a coating to avoid immune responses to implants.

This study presents new mathematical analysis expressions to a proposed PEO$_{10}$LiCF$_3$SO$_3$ based memory storage element with a new and modified equivalent circuit model (Song *et al*., 2000; Bi and Poo, 2001; Latham *et al*., 2000).

Background: Much of the interest in polymer electrolytes arises from their potential application in advanced charge storage technology. Particularly for

lithium anode storage, the dual requirements of high ionic conductivity and mechanical stability have been difficult to meet. One needs a polar polymer for lithium solubility, of high molecular weight for mechanical stability. Polyethylene oxide-PEO meets these criteria but its ionic conductivity is temperature dependent. The mechanism of ion conductivity in the PEO lithium salt system at room temperature is not fully understood. It has been established from that the lithium ions move mainly through the amorphous portions of the polymer, which are present at room temperature only because entanglement prevents full crystallization. Temperature and frequency dependence of the conductivity show that the lithium conductivity does not arise from a simple process of statistically independent lithium hops through a static polymer matrix, but that the dynamics of the polymer matrix are essential to the transport.

Ethylene oxide (CH_2CH_2O) 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 [$HO(CH_2CH_2O)nH$] 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. These polymer-alkali salts are recognized as fast ionic conductors with wide charge storage, which facilitate using them as solid electrolytes in batteries, chemical sensors and other applications (Ho *et al*., 2005; Judeinstein *et al*., 2005; Yu *et al*., 2005; Tao and Cummings, 2007; Blazejczyk *et al*., 2004). 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 neighbouring chains as the cation (Li+) forms ionic bonds with the negatively polarised 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 (Hehmeyer *et al*., 2007; Curtright *et al*., 2004; Moore and Schneider, 2001; Turcu *et al*., 2006; Anne-Valerie Ruzette *et al*., 2001; Mui *et al*., 2002) that ionic conduction in $PEO_xLiCF_3SO_3$ occurs by the cation (Li+) hopping between sites in either the single or double helix structures. Other studies showed the ionic conductivity occurs mainly in the amphorous phase rather than in the crystalline phase. Furthermore

experiments with dopant ions that form immobile ion pairs indicated that transport is not 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.

MATERIALS AND METHODS

Experimental arrangements: Polymer films were prepared using polyethylene oxide with average molecular weight of 5×106 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 h 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 min in an oven at 50°C. The produced devices were placed in a transistor housing which guarantees the ability to use them on electronic boards.

RESULTS

Device characterization: Complex impedance characterization is carried out to determine the device response. Figure 1 illustrates the complex impedance as a function of frequency.

Both real and imaginary parts of the complex impedance behave in a symmetrical but opposite manner where at any value within a range of frequencies the product of the real and imaginary parts is negative.
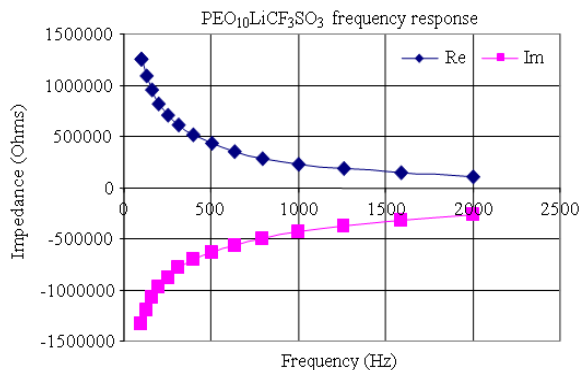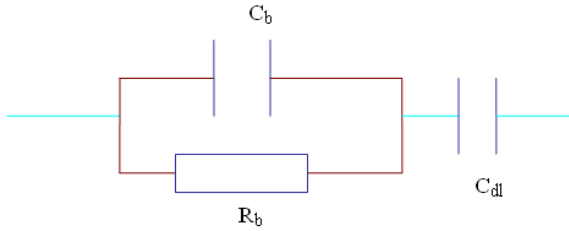

Fig. 1: Device frequency response

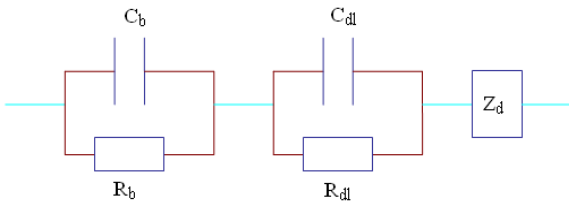Fig. 2: PEO$_n$LiCF$_3$SO$_3$ equivalent circuit model with blocking electrodes

Fig. 3: PEOnLiCF3SO3 equivalent circuit model with reversible electrodes

Equivalent circuit model: In practice ion-reversible electrodes for both cations and anions in PEOnLiCF$_3$SO$_3$ are not possible to make, hence, a sandwiched film of this solid polymer electrolyte will form between the electrodes. With a DC bias, a depletion layer of accumulated charges will form at the electrode-electrolyte interface inducing capacitive effect. As the charge builds up at the interface, new capacitance is formed by a double layer (C$_{dl}$). Upon applying an AC signal, a displacement of the applied potential and measured current is observed, which is caused by the bulk electrolyte Capacitance (C$_b$) in parallel with the bulk Resistance (R$_b$) used to determine ionic conductivity. Such blocking electrodes equivalent circuit model is shown in Fig. 2.

If the polymer film is placed between partially reversible electrodes that can react with either cation or anion, then additional elements should be added to the previous model to provide an ionically reversible system as shown in Fig. 3. The additional elements are double layer Resistance (R$_{dl}$) and diffusion impedance (Z$_d$) which is a function of ions mobilities as they pass through the formed double layer at the PEO$_n$LiCF$_3$SO$_3$-Ag interface.

DISCUSSION

As shown in Fig. 4, the real part is positive and decreasing with frequency while the imaginary part is negative and increasing with frequency, then a model which readily presents itself is a parallel combination
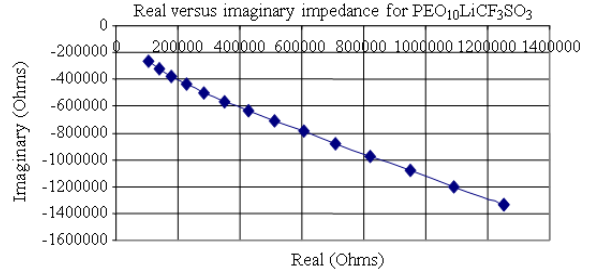

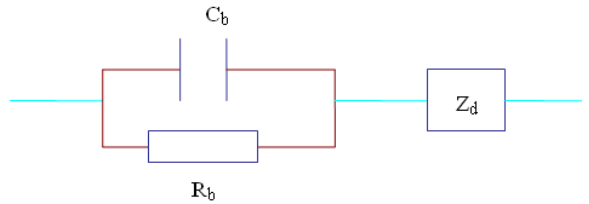Fig. 4: Relationship between real and imaginary impedances of PEO$_{10}$LiCF$_3$SO$_3$

Fig. 5: Suggested model for PEO$_{10}$LiCF$_3$SO$_3$ tested devices

of a resistor and capacitor with an effect of diffusion impedance (Z$_d$). No evidence of a double layer capacitance effect is realized as the plot representing the real versus the imaginary parts does not show a spur at low frequencies. Hence, the suggested equivalent circuit model based on this is shown in Fig. 5.

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

$$\frac{V_{out}(\omega)}{V_{in}(\omega)} = \left(\frac{\frac{1}{j\omega C_b}}{\left(\frac{1}{j\omega C_b}\right) + R_b} \right) = \left(\frac{1}{1 + j\omega C_b R_b} \right) \quad (1)$$

Multiplying by conjugate to obtain real and imaginary parts:

$$\left(\frac{R}{1 + j\omega C_b R_b} \right) = \left(\frac{1 - j\omega C_b R_b}{1 + \omega^2 C^2_b R^2_b} \right) \quad (2)$$

Then:

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

$$Im(Z) = -\left(\frac{\omega C_b R_b Z_d}{1 + \omega^2 C^2_b R^2_b} \right) \quad (4)$$
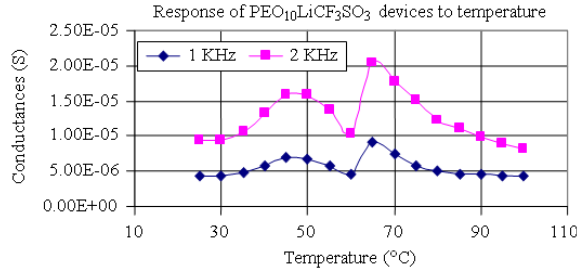
Fig. 6: Effect of Temperature on the conductance of $PEO_{10}LiCF_3SO_3$

However, when frequency response curves analyzed for these non-heat treated samples, it is found to have the mathematical expressions in Eq. 5 and 6 below:

$$Re(Z) = \left(\frac{Z_d}{1 + \omega^2 C_b^2 R_b^2} \right) \log\left(\frac{\omega_c}{\omega} \right) \tag{5}$$

$$Im(Z) = -\left(\frac{\omega C_b R_b Z_d}{1 + \omega^2 C_b^2 R_b^2} \right) \log\left(\frac{\omega_c}{\omega} \right) \tag{6}$$

where, ω_c denotes the crossing frequency of the zero frequency axis which marks the starting point of impedance polarity reversal. When this occurs, it is found that after this crossing point both real and imaginary curves will intersect at a frequency given by Eq. 7:

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

From Eq. 3-6, it is realized that the overall diffusion impedance has a logarithmic effect on the total impedance of the equivalent circuit. In other words frequency response of the device obeys a power law function. Hence the overall diffusion impedance is given by:

$$Z_{diffusion} = Z_d \log\left(\frac{\omega_c}{\omega} \right) \tag{8}$$

Now rewriting Eq. 5 and 6 in terms of (8) gives:

$$Re(Z) = \left(\frac{Z_{diffusion}}{1 + \omega^2 C_b^2 R_b^2} \right) \tag{9}$$

$$Im(Z) = -\left(\frac{\omega C_b R_b Z_{diffusion}}{1 + \omega^2 C_b^2 R_b^2} \right) \tag{10}$$

Equation 9 and 10 represent a modified High-Pass filter expression. This is supported by Fig. 1.

Figure 6 shows the effect of temperature on the conductance of a non-pre-heated device as an implicit function of frequency.

CONCLUSION

There is an obvious dependency of both the real and imaginary parts on frequency and temperature. Further, the presence of inflection points on the curves while changing their concavity as the temperature increases suggests a phase transition process to have occurred. A clear increase in conductance level as a function of signal frequency is also observed with phase changes due to the two-phase system present in the polymeric material. The high impedance shown at DC level indicates the ability to use such polymeric material for charge storage and switching applications.

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