IMPEDANCE STUDIES ON THE SYSTEM LiClO$_4$–MEEP

P. W. M. JACOBS, J. W. LORIMER*, A. RUSSER and M. WASIUCIONEK**

Department of Chemistry, The University of Western Ontario, London, Ont. N6A 5B7 (Canada)

Summary

Experimental impedance results on the system poly(bis(methoxy-ethoxyethoxide)phosphazene) (MEEP) plus LiClO$_4$ have been made, using Ni electrodes, over a wide range of temperatures (−50 °C to 80 °C), compositions (n = 2 - 30 in (MEEP)$_n$LiClO$_4$) and frequencies (0.1 mHz - 65 kHz). The data have been analyzed in terms of a model which includes two conduction paths: along the polymer chains and between the chains. Each of these paths may be simulated by a bulk resistance and a parallel dielectric capacitance. Since these paths do not extend right across the electrolyte these circuit elements act in series. Because the electrode–electrolyte contact is not perfectly smooth, there is, in addition, a constant phase element in series with the two parallel R, C networks. This equivalent circuit is capable of giving a good representation of the impedance data over a wide range of frequency, concentration, and temperature.

Introduction

Recent studies by Blonsky *et al.* have shown that poly(organophosphazenes) dissolve a variety of lithium salts (LiX) and that the conductivity of mixtures of one of these, poly(bis(methoxyethoxyethoxide)phosphazene), or MEEP, with LiX at room temperature is 2 - 3 powers of 10 higher than that of corresponding mixtures of poly(ethylene oxide), PEO [1]. The MEEP–LiX systems remain amorphous at temperatures from well below room temperature to a flow temperature of about 80 °C, while PEO–LiX complexes generally crystallize above room temperature. These properties make MEEP an ideal polymer for basic investigations of the fundamental properties of polymeric electrolytes.

This paper describes the measurement and interpretation of the impedance properties of MEEP–LiClO$_4$ mixtures over a wide range of temperature

---

*Author to whom correspondence should be addressed.

**Permanent address: Institute of Physics, Warsaw Technical University, Chodkiewicza 8, 02-525 Warszawa, Poland.

and composition. An extensive discussion of the conductivities in these systems will be given elsewhere. Only measurements with blocking electrodes (Ni) are given here; we have also made impedance measurements using non-blocking Li electrodes and these results will be given in a later paper, together with their interpretation in terms of a new theory of ionic transport in polymer electrolytes, which is presented at this conference [2]. Impedance measurements have been made previously on poly(ethylene oxide), e.g., refs. 3 and 4.

Experimental results

MEEP was prepared via reaction between previously polymerized $(NPCl_2)_3$ and sodium (methoxyethoxy)ethoxide, both dissolved in THF, in the presence of a catalyst (Bu_4NBr) [1]. The resulting polymer was extensively purified and its purity checked by IR and ^1H and ^{31}P NMR spectra.

Differential scanning calorimetry measurements (Perkin-Elmer DSC 1b) were carried out at scan rates of 10 K min^{-1}, in the temperature range 180 - 360 K, using samples of 5 - 15 mg sealed in aluminum pans. It was found that for $(MEEP)_n$–LiClO$_4$ complexes with $n \geqslant 20$ the glass transition temperatures, T_g, were close to that for pure MEEP (194 K) but with higher Li$^+$ concentrations they increased up to 233 K (for $n = 2$).

Films for conductivity measurements were cast directly onto a nickel electrode and dried until all traces of solvent or water disappeared (as shown by IR spectra). Conductivities were determined from a.c. complex impedance spectra, measured in the range 100 mHz - 65 kHz, using a Solartron 1250 Frequency Response Analyzer and Solartron 1286 Electrochemical Interface. Figure 1 shows the temperature-dependence of conductivity of an $(MEEP)_n$–LiClO$_4$ complex with $n = 12$. The data cannot be fitted by the Arrhenius equation but the VTF equation

$$\sigma T^{1/2} = A \exp\{-E/R(T - T_0)\} \tag{1}$$
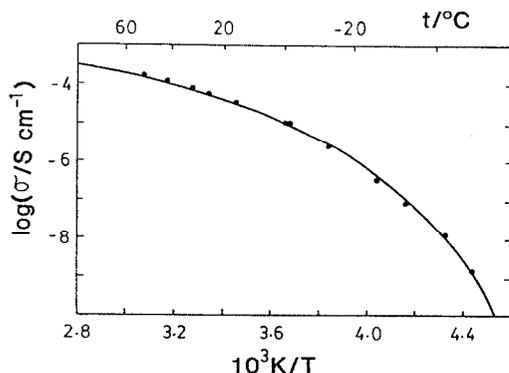
Fig. 1. Temperature dependence of the ionic conductivity of $(MEEP)_n$–LiClO$_4$ with $n = 12$. The continuous line shows the fit of the data to the VTF eqn. (1) with $A = 0.94$ S cm^{-1} K$^{1/2}$, $E = 7.7$ kJ mol^{-1} and $T_0 = 165$ K.

(with σ the conductivity) fitted the data extremely well over the complete temperature and concentration range studied (n = 2, 4, 6, 8, 12, 20, and 30). For low salt concentrations both A and the conductivity increase up to a maximum at n between 20 and 12 (or molality m = 0.18 - 0.29 mol kg^{-1}). For higher concentrations (m = 0.29 - 1.8 mol kg^{-1}) A decreases. A/m *versus* m is the more revealing parameter since this shows the subtle effects of increased Li^{+} concentration. (If the sole effect was to increase the carrier concentration A would rise linearly with m.) Changes in the energy parameter E follow the same trends with m as A, but relative changes in this case are much smaller. Changes in T_0 with m follow the same trend as T_g.

Typical impedance spectra for (MEEP)$_n$–LiClO$_4$ between blocking electrodes are shown in Fig. 2. The general characteristics of these spectra are:

(i) At high temperatures and high concentrations (Fig. 2(d)) the plot of —ImZ *versus* ReZ is a straight line inclined at an angle of about 60 - 85° with the real axis. This angle is independent of temperature for the same cell, but varies with the cell.
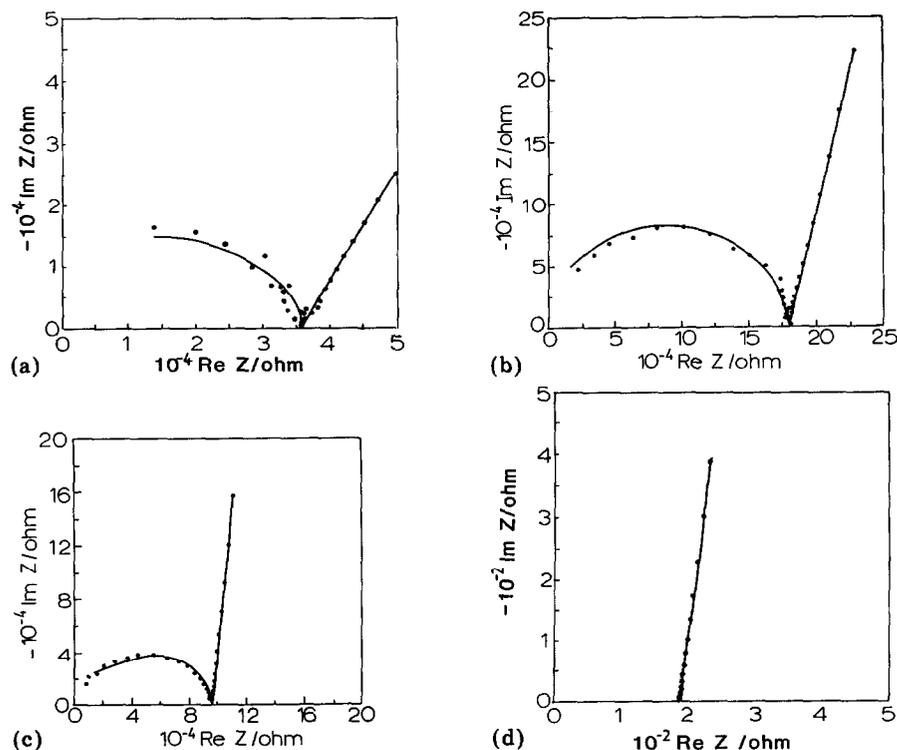
Fig. 2. Nyquist plots of —ImZ *vs.* ReZ in the frequency range 0.1 Hz - 65 kHz for (MEEP)$_n$–LiClO$_4$ between Ni electrodes. The frequency range plotted, and the frequency for which ImZ = 0, are given for each plot. (a) n = ∞ (pure MEEP) at 332 K. 3.66 Hz - 65 kHz; 206 Hz; (b) n = 20, at 253 K; 1.5 Hz - 65 kHz; 87 Hz; (c) n = 12, at 238 K; 0.87 Hz - 65 kHz; 116 Hz; (d) n = 4, at 313 K; 274 Hz - 65 kHz; 65 kHz.

(ii) As the temperature is decreased at constant n, or the concentration of $LiClO_4$ is decreased at constant T, a portion of a somewhat distorted semi-circle appears at high frequencies (Fig. 2(a) - (c)). This semicircle is never more than about 75% completed in the frequency range employed (0.1 Hz - 65 kHz).

(iii) This semicircle is always distorted and, at least, has a flattened appearance. It may be represented by the superposition of two semicircles with their diameters placed consecutively along the real axis.

(iv) Designating the semicircle that starts (in the sense of increasing frequency) at the intersection of the straight line with ReZ as 1, and the one that terminates at the origin as 2, for pure MEEP 2 is much larger than 1, but as the concentration of Li^+ increases, 1 dominates. (The conductivity of pure MEEP must be due to residual ionic impurities, possibly Na^+.)

Interpretation and discussion

Mechanism of ionic conduction in MEEP

We suppose that there are two possible conduction mechanisms. At low concentrations there are many more oxygen sites along the polymer chains than $Li^+ClO_4^-$ ion pairs, so that when an Li^+ ion coordinates to an oxygen atom, there is a high statistical probability of the neighbouring oxygen sites being vacant (that is, not occupied by an Li^+ ion). We further suppose a dynamic equilibrium between bound and unbound Li^+ ions with a certain characteristic relaxation time. The ClO_4^- counter ions are presumed to be part of the ion atmosphere around each Li^+ ion. Even for $n = 2$ (n is the $P:Li^+$ ratio) there are 12 oxygen sites for every Li^+ and even though binding to adjacent O sites on the same side chain would lead to strong Li^+-Li^+ repulsions, and therefore be energetically unfavourable, a Li^+ would be able to make successive hops to several chains before finding its path blocked, when it must wait for the Li^+ blocking its path to migrate along the chain or to "desorb" or, alternatively, it must itself dissociate from the O site and become one of the interchain Li^+ ions. Thus we expect relatively high Li^+ conductivity along chains. The chain conductivity would at first increase with Li^+ concentration, m (increasing number of carriers), and then decrease with further increase in m due to enhanced probability of the blocking of migration paths. One reason for the relatively high conductivity of MEEP compared with PEO is now clear; in PEO the O atoms are part of the backbone and $n = 2$ in PEO means that every second O site is (on average) occupied. The situation in MEEP is similar, *i.e.*, one Li^+ per every second P atom, and if we assume that only one Li^+ can be bound by each pair of alkoxy side chains, there are still many vacant O sites at $n = 2$. In addition, the MEEP backbone is more flexible, which facilitates both hopping along chains and interchain migration of Li^+ ions.

The bound Li^+ ions we suppose to be in dynamic equilibrium with the inter-chain electrolyte. Li^+ between the chains migrate much as they would

in any reasonably concentrated ionic solution, with the polymer playing the role of the solvent. The motion of an Li^+ between the chains is impeded by the ionic atmosphere that surrounds it and by the O atom "traps" along the chain at which it may become adsorbed. So, again, the conductivity would be expected to increase with m at low m and then to decrease at high m. This is the experimental result, with the conductivity passing through a maximum at n between 20 and 12.

Equivalent circuit

We do not at present have a sufficiently detailed microscopic model to estimate relaxation times for the two conduction paths, but the experimental results indicate that τ_1, τ_2 do not differ by more than a factor of about 10. Each conduction path is represented by a resistance R in parallel with a capacitance C. Superficially, it might appear that these two circuit elements should be in parallel, but this is not so, for the polymer does not form linear chains extending continuously across the electrolyte from one electrode to the other. Rather does it form a twisted network so that an Li^+ ion migrates by hopping along a chain, then becoming desorbed and migrating between the chains for a while, then becoming re-adsorbed and migrating by hopping once again. Thus, our microscopic model really corresponds to a sequence of a large number of parallel R, C elements in series. These have but two relaxation times τ_1, τ_2 and so the equivalent circuit for bulk transport is approximated by just two R, C elements in series.

The ideal non-blocking electrode–electrolyte interface may be represented electrically by a single capacitor that corresponds to the double layer. However, the nickel electrode–polymer interface is certainly not microscopically smooth. Such rough interfaces may be supposed to possess the property of self-similarity. We do not know how closely the nickel–polymer interface resembles an ideal Von Koch interface, but we presume that this may be a useful approximation. It follows from the work of Le Méhauté [5] and others [6 - 9] that a blocking interface with a particular fractal dimension exhibits an impedance

$$Z_i = A(j\omega)^{-\alpha} \tag{2}$$

The impedance Z_i has a constant phase angle ($ImZ/ReZ = \alpha\,\pi/2$, a constant independent of frequency ω) and so the circuit element giving rise to this behaviour is called a constant phase element (CPE). The slope of the linear segments in Fig. 2(a) - (d) is $\tan(\alpha\,\pi/2)$. Our complete equivalent circuit used to model the impedance of a cell consisting of $(MEEP)_n–LiClO_4$ between Ni electrodes thus consists of two R, C elements in series representing the bulk electrolyte, in series with a CPE which represents the rough electrode–electrolyte interface. If this may be approximated by a striated surface that has a cross-section which is a Von Koch interface, then the interface has a fractal dimension $1 + d_f$, where d_f is the dimension of the Von Koch curve [9]. However, α is not necessarily related directly to d_f despite proposals [6, 7] that

$$\alpha = 3 - d_f \tag{3}$$

or

$$\alpha = 1/(d_f - 1) \tag{4}$$

The correct relation [7] between α and d_f for Von Koch geometry is

$$\alpha = (1/d_f) \log N / \log P \tag{5}$$

where N is the number of segments of length L/P in a line of total length L. If each section between the N segments is broken into M segments in the n repetitive operations leading to self-similarity, then

$$d_f = \log(M + N)/\log P \tag{6}$$

α thus depends uniquely on M, N and P, but an experimental determination of α unfortunately is of little help in characterizing the geometry of the interface. Despite this difficulty, we accept that a non-smooth electrode–electrolyte interface may be represented by a CPE, and we apply the resulting equivalent circuit (Fig. 3) to the calculation of the impedance of our cell. Calculated impedances in the Nyquist representation are shown as continuous lines in Figs. 2(a) - (d). These agree quite well with the experimental curves and show that this equivalent circuit, which is based, however qualitatively, on microscopic models, is capable of representing the range of impedance spectra found. No doubt the agreement with experiment could be improved by non-linear least squares (NLLS) fitting and we shall therefore reserve quoting parameter values and a discussion of relaxation times until such NLLS fitting has been completed.
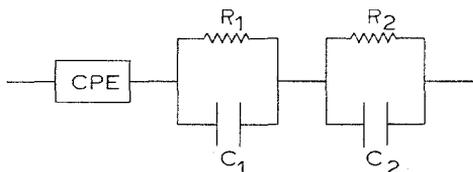
Fig. 3. Equivalent circuit used to simulate the electrochemical cell $Ni|(MEEP)_n$–$LiClO_4|$·Ni.

Acknowledgement

References

1 P. M. Blonsky, D. F. Shriver, P. E. Austin and H. R. Allcock, *Solid State Ionics*, *18/19* (1986) 258.

2 J. W. Lorimer, *J. Power Sources*, to be published.
3 D. Fauteux, *Solid State Ionics, 17* (1985) 133.
4 F. Boniino, M. Ottaviani, B. Scrosati and G. Pistoia, *J. Electrochem. Soc., 135* (1988) 12.
5 A. Le Méhauté and G. Crépy, *Solid State Ionics, 9/10* (1983) 17.
6 S. H. Liu, *Phys. Rev. Lett., 55* (1985) 529.
7 L. Nyikos and T. Pajkossy, *Electrochim. Acta, 30* (1985) 1533.
8 M. Keddam and H. Takenouti, *C. R. Acad. Sci. (Paris), II 302* (1986) 281.
9 M. Keddam and H. Takenouti, *Electrochim. Acta, 33* (1988) 445.