MEASUREMENT OF TRANSFERENCE NUMBERS IN POLYMER ELECTROLYTES

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Abstract

This paper describes the development of a technique for evaluating the transference number of mobile species in polymer electrolytes. The procedure used originates in a modified Hittorf method [1] with the application of an appropriate cell configuration, electrolyte support, assembly strategy and analytical method. In accordance with the convention applied to poly(ethylene oxide) based polymer electrolytes, the value of **n** indicates the number of repeat units of the polymer per guest salt cation in an electrolyte composition given by EO_nLiClO_4. Measurements were carried out on the system based on poly(ethylene oxide), PEO, and lithium perchlorate, with compositions of n between 5 and 100.

Keywords solid polymer electrolyte, transference numbers, Hittorf technique

Introduction

Since the introduction of the first examples of the class of "polymer electrolytes" in 1978 [2], there has been an intense interest in lithium salt based systems motivated by the promise of commercial applications in high energy density primary and secondary batteries. In the years which followed the exploratory studies of this new class of materials, many host polymers with improved properties were developed and electrolytes based on a remarkably wide range of guest ionic species were characterised using a variety of techniques. The results of these studies have been extensively reviewed [3-6] and have led to the conclusion that the properties of the host polymer, the nature and concentration of the guest ionic species, the preparative conditions and even the thermal history of the sample, have a dramatic effect on the behaviour of the resulting electrolyte.

The current view of the charge transport in polymer electrolytes is that the motion of ions takes place through the amorphous fraction of the polymeric medium and involves ion transfer by short range movement of chain segments and the redistribution of charged species between temporary coordination sites. Various techniques have been applied to the study of the mobile species in polymer electrolytes [7-17] and although rather inconsistent results have been obtained with different methods it has become clear that the participation of individual species or ion aggregates is greatly influenced by the nature of the salt and polymer, the concentration of the guest species and the presence of plasticising agents or solvent residues.

Most electrolytes proposed for applications in advanced solid-state lithium based galvanic cells have only been characterised in terms of their total ionic conductivity measured with ac techniques. When a continuous current is passed through a cell a significant contribution to the voltage over the electrolyte arises when the transport number of the lithium ion is less than unity. Several authors recognised the importance of this aspect of polymer electrolyte performance and different techniques have been applied with the objective of developing a convenient method for estimating the contribution of the constituent ions to the charge transport process and eventually optimising the electrolyte composition for practical applications.

In 1982 Sorensen [7] and Steele [8] proposed the use of ac techniques to characterise the transport number of a lithium salt based electrolyte. Subsequently PFG-NMR methods [9, 10], tracer diffusion [11], limiting current measurements [12], Tubandt [13], emf measurements [14], potentiostatic polarization experiments [15] and transient ionic current techniques [16] were successively applied. Each of these techniques has advantages but also suffers from characteristic difficulties. The application of ac techniques for example, is complicated by the difficulty in identifying the necessary impedance contributions [17] and eliminating the effect of the passivating layer formed on the non-blocking lithium metal electrodes [20]. NMR and radiotracer diffusion measurements, based on the assumption that the salts are completely dissociated in the low dielectric constant polymer medium, give rise to incorrect estimates of transport numbers. The Tubandt method seems to provide a simple, elegant solution to the problem posed, however the application of this procedure to the majority of polymer electrolytes is not feasible because of the practical difficulties involved in separating adjacent electrolyte compartments. While the Hittorf technique is similar in practical aspects to the Tubandt method, it differs in that the active ion content is estimated by analysis of the compartment contents rather than simply weighing the

separated sections of the cell. In this respect the Hittorf technique may, in principle at least, be applied to even highly amorphous, elastomeric materials.

Experimental

i) **Film preparation** - In recognition of the influence of water on the behaviour of polymer electrolytes based on hygroscopic salts [18], the components of the polymer electrolyte were dried and stored in a high integrity argon filled glovebox. The lithium perchlorate (Merck, pro analysis) was dried at 180ºC under vacuum, cooled and ground at room temperature then subjected to a final thermal treatment at 400ºC. The polymer (Aldrich, Mw 5 x 10^6) was heated under vacuum at 55ºC for at least 7 days. As the configuration of the cell used for transference number measurements required the production of an electrolyte block with a thickness of about 2mm, the hot pressing method developed by Gray [19] was adapted to the use of a 25mm diameter stainless steel die. Appropriate masses of dry salt and polymer were transferred to an agate ball mill and ground at room temperature to produce finely divided homogeneous mixtures with compositions of n between 5 and 100. Electrolyte blocks were prepared by transferring an appropriate weight of material to the die and applying an initial pressure of 200 kg cm^{-2} briefly, then releasing the pressure and raising the die temperature to 100ºC during 45 minutes. The electrolyte was allowed to cool in the die overnight and was later removed as a homogeneous disk. An electrolyte block (20 x 10mm) was cut from this disk and located in the Hittorf cell support, illustrated in Figure 1. a). Part b) of this figure illustrates the schematic division of the electrolyte block into four compartments.
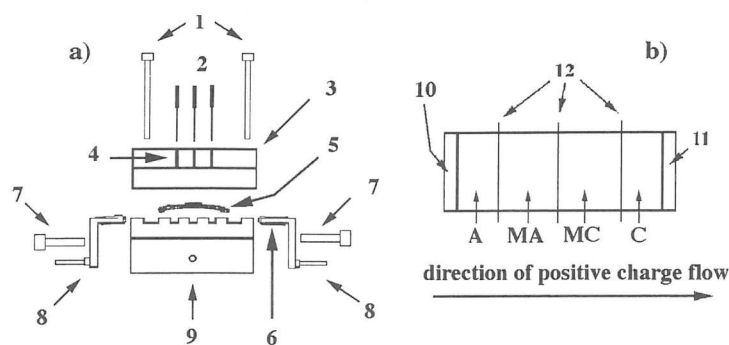

Fig. 1. a) Cell support developed for the transference number measurements (1 and 7 assembly screws, 2 sectioning blades, 3 top cover, 4 blade slots, 5 electrolyte block, 6, 10 and 11 electrodes, 8 electrode support, 9 base). **b)** Diagram of the electrolyte sections referred to in the text (12 compartment frontiers)

ii) **Cell assembly** - The assembly of the cell was completed by applying appropriate electrodes to the electrolyte block and heating the cell and support to 120ºC in a tube oven (Buchi TO51) for at least 24 hours. At this temperature the sample was completely amorphous. A constant current (PAR model 363 galvanostat/potentiostat) was passed through the cell for a known interval of time and the variation of the cell potential recorded automatically with a DVM (Keithley model 197). After an appropriate period the current was interrupted and the electrolyte block was sectioned, by applying the thin knife blades, indicated in Figure 1a) into the slots in the top cover of the cell support. The electrolyte sections were then separated, weighed and analysed.

iii) **Lithium and lead analysis** - The preparation of solutions containing samples from the electrolyte compartments was carried out using 30 mL Kjedhal flasks within a fume cupboard, by dissolving approximately 50 mg of each section in about 15 mL of warm distilled water, adding 3 mL of concentrated sulphuric acid and 0.5 mL of concentrated perchloric acid (70% w/w). Each sample was heated slowly until the HClO$_4$ began to decompose with the evolution of white fumes and the polymer digest changed from brown (charred polymer) to yellow. The solution was decolourised by vigorous heating only after the evolution of fumes had ceased. The digest was allowed to cool to room temperature and the contents of the Kjedhal flask were transferred quantitatively to a 100 mL volumetric flask.

Solutions were prepared from high purity Li$_2$CO$_3$ dried at 110 ºC and automatic pipettes were used to produce a set of acid matrix-matched Li standards. The analysis of the samples was carried out using a Thermo-Jarrel-Ash model Video 22 atomic absorption analyser at 670.8 nm with a 0.5 nm slit width.

Lead analysis was carried out using a similar method with appropriate standard Pb^{2+} solutions prepared from lead acetate and analysed at 283.3 nm.

Results and discussion

Given the spectroscopic evidence [21 - 23] for the presence of charged and uncharged aggregates, and that the latter may also contribute to the transport of species through polarised electrolytes [24], it must be concluded that most of the experimental methods are unable to separate the effects of contributions from each of the species which are present in the electrolyte. In accordance with previous results reported in the domain of aqueous electrolytes, the use of the transport number must be substituted by the transference number which admits the presence of mobile ion aggregates.

The concept of transference number, as applied to a representative uni-univalent salt, MX, composed of two constituents, M$^+$ and X$^-$, was defined by Spiro [25] as the net number of Faradays carried by a constituent ion as a result of the movement of all species containing the ion through an imaginary reference plane perpendicular to the direction of the current flow when one Faraday passes through the plane. In practical terms this means that the transference number includes contributions from all the charged species which contain the constituent in question. In the case of the salt considered above, the species X$^-$, MX, M$_2$X$^+$, MX$_2^-$ and M$^+$ may all be influenced by the passage of current through the cell and measurements of concentration changes caused by the current will reflect the cumulative effect.

The principal difficulties in applying the Hittorf method to polymer electrolytes are associated with the optimisation of the analytical procedure and the behaviour of the anode and cathode/electrolyte interfaces. Previous attempts to obtain consistent analytical results involved a similar wet digestion technique [26] and the use of a microwave heating procedure [27], however a significant dispersion of analytical results was observed which frustrated attempts to reproduce experimental results. Our optimisation of the conditions of the wet digestion resolved these problems and a good correlation between experimental and calculated values was obtained. Figure 2 is included to illustrate the results obtained with powder and pressed disk samples.
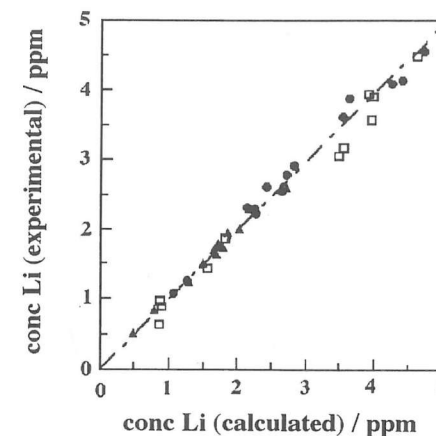

Fig. 2. Correlation between experimental and calculated Li content (powder samples ▲, pressed electrolyte ● and electrolyte block off-cuts ☐)

In the Hittorf method a constant current is passed through the electrolyte block during a known interval of time. The current flow is then interrupted and the electrolyte sectioned, creating

the anode (A), middle anode (MA), middle cathode (MC) and cathode (C) compartments, illustrated in Figure 1b). The contents of the various compartments are analysed for the species M and simple relationships [28] may be derived to calculate the transference number. In practical terms the quantity of charge passed through the electrolyte must be appropriate for the dimensions of the cell and the location of the compartment frontiers to ensure that the concentration change caused by the current is restricted to the anode and cathode compartments. If the middle anode and middle cathode compositions are alterred during the experiment then the corresponding concentration change of the anode and cathode electrolyte sections will not give an accurate value of the transference number. The expected alterations in the lithium and lead distribution, as a result of charge transport, are shown in Figure 3 and 4 for the two cell configurations studied.

In exploratory studies [27] based on a symmetrical Li|PEO$_8$ Li ClO$_4$|Li cell configuration Bruce reported difficulties in the separation of lithium metal anodes and cathodes from the adhesive surfaces of the anode and cathode electrolyte sections. Clearly any lithium transfer between the electrode and electrolyte compartments during the cell sectioning procedure introduces significant errors into the transference number measurement. This limitation of the original cell configuration led Bruce and coworkers to substitute the lithium cathode by lead foil with the objective of creating a more mechanically robust catholyte/cathode interface. This solution was reported to be at least partially successful.

In the present study cells were assembled with a new symmetrical Pb|PEO$_n$LiClO$_4$|Pb configuration. It was expected that this new assembly would allow more precise measurements to be made, in particular on the anolyte, the electrolyte section in contact with the anode. The presence of the lead anode was expected to result in the transference of lead ions to the anolyte and therefore a net reduction in the amount of lithium would be observed. As Pb^{2+} ion mobility was expected to be low, species transferred from the anode to the anolyte were expected to remain in the anolyte, as shown schematically in Figure 3c). Figure 3c) shows the chronopotentiometric curves registered during experiments with a range of electrolyte compositions. The observed behaviour was erratic and irreproducible. The current efficiency of the electrode processes was estimated by analysing the lead content of the anolyte and the lithium content of the cathode. In both cases the efficiencies were lower than expected (Table 1) and suggested that part of the current passed through the cell was not associated with the transport of lithium or lithium-containing aggregates. In view of the increasing resistance of the electrode/electrolyte interface it seems reasonable to attribute part of the current to electrolytic degradation. The results of these experiments allow us to eliminate the

symmetrical cell as a valid configuration for the transference number measurements of lithium salt based electrolytes.

The difficulties experienced with the use of a lead anode resulted in a return to the asymmetric Li|PEO$_n$LiClO$_4$|Pb within an oxygen-free argon filled glovebox. Analysis of the results of typical experiments, included in Figure 4, demonstrated that this cell configuration resulted in a much more uniform and reproducible chronopotentiometric response. While the use of this cell configuration resolved the problems encountered at the anode interface, the nature of the interface between the amorphous, adhesive polymer and the mechanically fragile lithium anode surface meant that the transfer of metal across the interface greatly influenced the value of the transference number calculated from the anolyte analysis. Consequently these results could not be used to calculate transference numbers.

Although the performance of the lead cathode was not ideal, analysis of the lithium transfer to the cathode did confirm that efficiencies higher than 90% could be achieved. The advantage of including the analysis of the lithium content of the cathode alloy in the experimental procedure is that the value obtained may be used to correct the transference number obtained, based on the assumption that the lithium not transferred was removed mechanically to the catholyte. At low cell currents the efficiency of the cathode reaction was found to be close to 95%. Experiments carried out under these conditions confirmed that the transference number of lithium is approximately 0.5 in an electrolyte with composition EO$_{15}$LiClO$_4$. While this experimental assembly is not entirely satisfactory and further experiments are being carried out to demonstrate the reproducibility of the results and explore the effect of salt concentration on the transference number, the current results are in reasonable agreement with those published for a similar electrolyte based on poly(ethylene oxide) and lithium triflate [29].

Table 1. Typical results of the Li and Pb analysis of cell compartments.

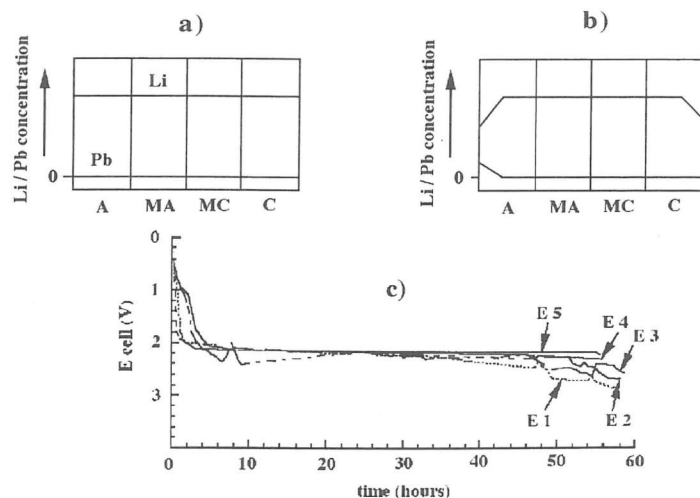| Experiment	1	2	3	4
% Li deposition	86.6	34.8	29.9	88.1
% Pb dissolution	20.4	35.7	52.2	37.7

Fig. 3. Schematic diagram of the Li and Pb distribution; a) initial b) final. c) Chronopotentiometric profile observed during current flow through the Pb|PEO$_n$LiClO$_4$|Pb cell.
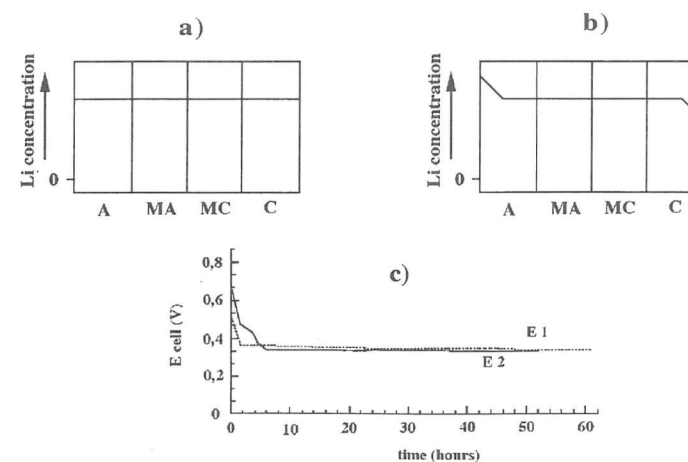

Fig. 4. Schematic diagram of the Li distribution; a) initial, b) final. c) Chronopotentiometric profile observed during current flow through the Li|PEO$_n$LiClO$_4$|Pb cell cell.

Conclusions

The development of a reliable method for assessing the transference number of polymer electrolytes is of such importance that experiments are also being directed toward the use of composite electrodes based on intercalation compounds. Materials such as $Li_xMn_2O_4$, are expected to be suitable for application as anodes and cathodes of a symmetrical Hittorf cell as they can sustain high diffusion of lithium ions and incorporate large concentrations of guest lithium species within their structure. Using this new cell configuration and the analytical technique described in the experimental section, accurate values of the initial and final lithium contents of the anode, the cathode and the composition of the surrounding electrolyte material in the composite electrodes may be obtained. The difference between the initial and final compositions of these components should allow us to obtain more reproducible estimates of the transference numbers based on the alterations in both anode and cathode compartments of the cell.

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IONIC CONDUCTIVITY STUDIES AND THERMAL BEHAVIOUR OF POLY(ETHYLENE OXIDE) - La (ClO4)3 ELECTROLYTE FILMS

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Abstract

Polymer electrolytes based on a poly(ethylene oxide) host with trivalent cation guest species have been prepared by the solvent casting method and characterised by conductivity measurements and thermal analysis. Electrolytes with compositions in the range of n between 5 and 120 were found to behave in a manner similar to that previously observed with lanthanum trifluoromethanesulphonate based systems. The total ionic conductivity of these materials is close to other trivalent cation based systems (approximately 10^{-3} Ω cm^{-1}) and, as expected, the thermal stability of the electrolyte is limited by the presence of the perchlorate anion.

Keywords - solid polymer electrolyte, poly(ethylene oxide), thermal stability, ionic conductivity

Introduction

Since 1978, when Armand presented polymer electrolytes as a new class of solid ion-conducting phase, the development of these materials has attracted considerable interest. Polymer electrolytes may be conveniently defined as solvent-free, solid polymer films, frequently of semi-crystalline morphology, which contain dissolved guest salts and form ionically conducting phases [1, 2]. The electrolytes produced from the most comprehensively studied host, poly(ethylene oxide), PEO, are normally of mixed morphology and show behaviour which is very different from that of conventional crystalline solid electrolytes and aqueous or non-aqueous liquid electrolyte media. In polymer electrolytes the transport process takes place exclusively in the amorphous phase and involves the short range movement of chain segments and the redistribution of the mobile ionic species between temporary sites available in the liquid-like environment.

While the principal motivation for polymer electrolyte research continues to be provided by the promise of highly conductive electrolytes/separators for applications in all-solid-state advanced batteries, during the last five years novel applications for flexible polymer electrolytes have been described in sensors, electronic components or optical display elements. The potential for the development of commercial devices has stimulated sustained intense research directed towards the characterisation of materials based on mono, di and trivalent salt systems [2, 3].

The electrolyte system which is described in this paper was prepared by using a modified reflux procedure [4] to dehydrate the guest salt, lanthanum perchlorate. Thin films of electrolyte were produced by deposition from a homogeneous solution of salt and host polymer. Measurements of the ionic conductivity and thermal behaviour of semi-crystalline solids with a wide range of guest salt concentration have been used to characterise the behaviour of the resulting solid electrolyte.

Experimental

The presence of water molecules in polymer electrolytes may enhance or inhibit the ionic conductivity and therefore, in the majority of studies, the influence of water is reduced by drying the electrolyte components and preparing the electrolyte films in anhydrous conditions. PEO (Aldrich, Mw 5 x 10^6) was dried under vacuum for 7 days at 55°C and stored under an inert atmosphere inside an argon-filled drybox. Partially hydrated lanthanum perchlorate (Johnson Matthey, 99.9%) was subjected to a drying procedure previously described by Gray [4]. In accordance with this procedure a known mass of the salt was transferred to a round bottomed flask and dissolved in approximately 30 mL of acetonitrile (Aldrich, HPLC grade). At this stage a known weight of lanthanum perchlorate was removed from the same sample bottle for analysis using a conventional volumetric technique [5]. A modified Soxhlet extractor, with regenerated molecular sieves in the extraction volume, was adapted to the flask and the contents heated to initiate reflux. The water initially associated with the salt was substituted by solvent molecules and was removed by passage through the molecular sieve column during reflux. The concentration of water in the acetonitrile was monitored by removing samples for FTIR analysis and found to reach a minimum after approximately three hours, in accordance with the results reported by Gray in exploratory studies. The volume of the acetonitrile solution was then reduced by evaporation and the flask was sealed and transferred to a preparative drybox. An appropriate mass of the host polymer was added