

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 $\text{Li}_x\text{Mn}_2\text{O}_4$, 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) - $\text{La}(\text{ClO}_4)_3$ 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 $10^{-3} \Omega \text{ cm}^{-1}$) 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 5×10^6) 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

to the salt solution to give a known electrolyte composition. This electrolyte composition is conveniently defined by the parameter, n , the number of polymer repeat units per cation (n is also therefore the ratio O/La^{3+}). All subsequent operations involving the manipulation of electrolyte components, the preparation of samples for conductivity measurements and thermal analysis, were carried out under a dry argon atmosphere within high integrity gloveboxes. After prolonged stirring the homogeneous solution of polymer and salt was transferred to a teflon mould and the solvent was evaporated within a sealed compartment located inside a preparative argon-filled glovebox. The mould supporting the resulting polymer film was transferred to a Buchi TO51 tube oven and subjected to a final drying process at 50 °C for 72 hours under vacuum to remove solvent residues.

The total ionic conductivities of samples was determined by locating an electrolyte disk between two 10 mm diameter ion-blocking gold electrodes. The electrolyte/electrode assembly was secured in a suitable constant volume support which has been previously described [6]. The cell support was located in a Buchi TO51 tube oven and the sample temperature was measured by a type K thermocouple positioned close to the electrolyte disk. The bulk conductivities of electrolyte samples were obtained during heating cycles using the complex plane impedance technique (Schlumberger Solartron 1250 frequency response analyser and 1286 electrochemical interface) over a temperature range of between 25 and 100 °C and at approximately 7 °C intervals.

Open platinum cans were used to support the electrolyte samples during thermogravimetric analysis (TGA). The electrolyte samples, in the form of 5mm diameter disks, were removed from electrolyte films within the glovebox. The samples were transferred to the cans and located within the thermobalance with the shortest possible exposure to the laboratory atmosphere. Analysis took place under a flowing nitrogen atmosphere at a heating rate of 10 °C min⁻¹ using a Perkin Elmer TAC 7/DX controller with a TGA 7 furnace operating at temperatures between 30 and 500 °C.

Disk sections of between 5 and 10 mg mass were removed from electrolyte films and sealed within 40 μ l aluminium DSC cans inside a preparative glovebox. The purge gas used in all the analyses performed was high purity argon supplied at a constant 35 cm³ min⁻¹ flow rate. Thermal analysis by heat-flux DSC was carried out with a Mettler TC11 controller and a model DSC 20 oven equipped with a cooling accessory. All samples were subjected to a 5 °C min⁻¹ heating rate and were characterised between -40 and 500 °C.

Results and discussion

In order for the guest salt to dissolve into the polymeric solvent and form a polymer electrolyte, the interactions between the ionic components of the salt and the polar groups of the polymer host must be energetically and entropically sufficiently favourable to compensate for the destruction of the salt lattice and the cohesive forces between polymer chains. There are many salts and polymers [3] which fulfill the necessary conditions for homogeneous solid state solutions to be formed between the components and clearly there are several factors which contribute to produce a favourable energetic balance in these systems. Generally an overall reduction in the free energy of the system occurs when the salt lattice energy and the polymer cohesive energy are low and the interaction between the cation or anion and the host polymer is strong. The nature of the host polymer, its ability to adopt convenient conformations which maximize the number of interactions with the guest species and minimize the distance of separation of the ions from the coordinating atoms in the polymer chain and even the dielectric constant of the polymer environment, are critical in creating the appropriate conditions for the formation of a solid electrolyte solution with suitable charge carrier concentration and mobility.

The hard-soft acid-base principle was originally introduced by Pearson [7] as a means of explaining observed stabilities of complexes formed between Lewis acids and bases and as an aid in predicting the stability of novel systems. In general a preference is found for complexes to be formed between hard acids and hard bases or between soft acids and soft bases. Within this scheme of classification the PEO macromolecule may be regarded as being a chain of suitably separated heteroatoms which act as hard bases. The lanthanides are classified as hard acids and therefore might be expected to form fairly stable complexes with macromolecules like PEO and show moderate ionic conductivity. Salts which form strong complexes with the macromolecular host will be readily solubilized but should have low conductivity as the cation is immobilised within the ion-polymer complex. The existence of a strong interaction between the cation and the polymer host does not necessarily result in an electrolyte with low total ionic conductivity; the electrolyte may also transport charge through the transference of anions between suitable coordination sites within the polymer structure.

Several electrolytes based on the lanthanide metals have been characterised [8 - 12] and found to show moderate ionic conductivity, although the mechanism, involving cations, anions or mixed species transport, has not yet been clarified. Electrolytes based on the lanthanide perchlorates have only been subjected to exploratory studies [4, 8, 9], partly due to the difficulty in drying the unstable salts and subsequently maintaining them in a constant and well-defined hydration state. The perchlorates of various cations are an interesting basis for polymer electrolytes as they are readily solubilized by the PEO host and form amorphous solutions over a wide range of electrolyte compositions.

The total ionic conductivities of electrolytes based on the $PEO_nLa(ClO_4)_3$ system are illustrated in Figures 1 and 2. As may be confirmed by comparison of this behaviour with that found with electrolytes based on the triflate salt of lanthanum [6], the conductivity observed is of a similar magnitude. In both these systems the conductivity is almost constant over the entire range of compositions studied and in this respect is quite different from the behaviour of conventional liquid electrolytes. Salt-rich electrolytes, with values of n between 5 and 20, show non-linear behaviour in their temperature dependence of conductivity. This behaviour is taken to be indicative of the presence of an amorphous morphology while linear behaviour is characteristic of a material in which an excess of uncomplexed PEO is present. Often linear variation of the temperature dependence of conductivity is accompanied by a change of gradient at the temperature of fusion of the polymer spherulites.

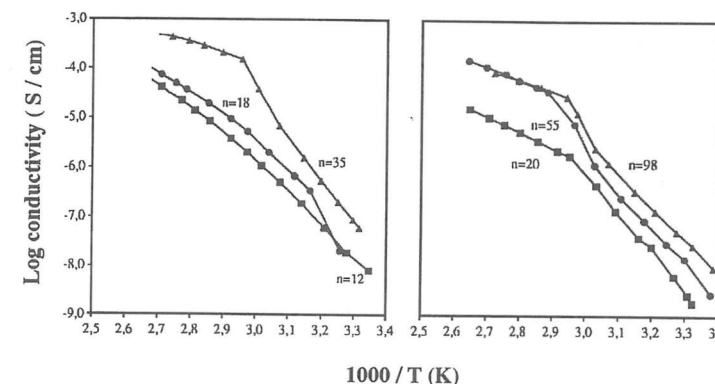


Fig. 1. conductivity behaviour of various electrolyte samples

The moderate ionic conductivity of electrolytes with salt rich compositions can be explained by the interaction of the guest salt species with the heteroatoms of the polymer chain segments. The existence of many interactions results in the formation of temporary ionic crosslinks between polymer chain segments and restricts the short range segment motion which is essential for ion transport. Under these conditions another aspect which may be important is the fact that in a media of such low dielectric constant an appreciable amount of ion association might be expected. The formation of ion aggregates would naturally be expected to reduce the ion mobility, contributing to a lower total ionic conductivity in this range of concentration. As the guest species concentration is decreased, with an increase in n , an optimum conductivity is observed. At this concentration the presence of fairly high concentrations of salt results in the suppression of crystallisation of the polymer host and as the amorphous fraction of the electrolyte is maximised the ionic conductivity is also high. Further reduction in the salt concentration causes an increase in the formation of polymer spherulites as the salt is expelled from the growing polymer spherulites and the increasingly convoluted conduction pathway, or the increasingly rigid electrolyte media, causes a reduction in conductivity. As the salt concentration is reduced the tendency to form ion aggregates is also decreased, resulting in an increase in the number of dissociated ions which have a higher mobility. The quantitative description of the changing characteristics of the electrolyte media is difficult, and a more complete interpretation of the detailed variation of conductivity may only be possible when

more systems have been characterised, however spectroscopic [13] and thermal evidence does exist to support the qualitative description presented.

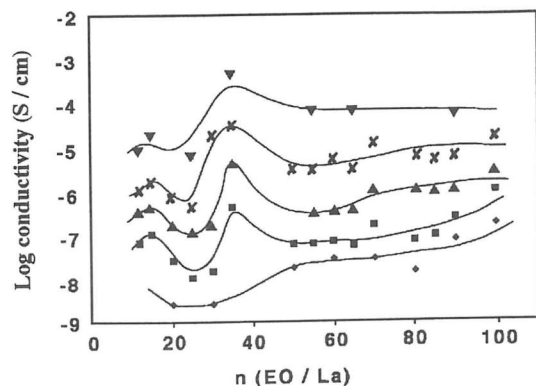


Fig. 2. conductivity isotherms for electrolyte compositions of n between 5 and 100 (◆ 30°C, ■ 40°C, ▲ 50°C, × 60°C, ▼ 100°C)

The results of the thermal analysis of samples of a range of electrolyte composition are illustrated in Figure 3. As expected from previous studies of lanthanide containing polymer electrolytes with low salt concentrations, and other perchlorate salt based polymer electrolytes, both endothermic and exothermic events are observed. At electrolyte compositions with n greater than 25 the endothermic peak registered at temperatures close to 60 °C is assigned to the fusion of the

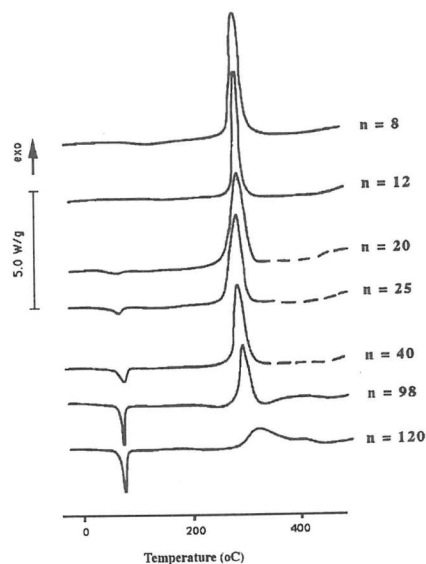


Fig. 3. DTA behaviour of selected electrolyte compositions

polymer spherulites and the exothermic event at about 300 °C is associated with the oxidative degradation of the polymer macromolecule. The area of the former peak decreased as the amount of added salt was increased, supporting the suggestion that the added salt eventually impedes the formation of polymer spherulites leading to the formation of a highly amorphous material when n is close to 20. No evidence was found for the formation of a crystalline complex between the polymer host and the europium perchlorate guest species.

The presence of the perchlorate salt in the polymer results in a significant destabilization of the host polymer. The electrolytes studied undergo a rapid, almost explosive, decomposition at temperatures close to 320 °C, in agreement with the results reported by Costa et al [14] in their studies of the electrolyte system based on PEO with lithium perchlorate. The thermogravimetric analysis results, illustrated in Figure 4, confirm that an increase in salt content gives rise to an expected decrease in the thermal stability of the polymer electrolyte.

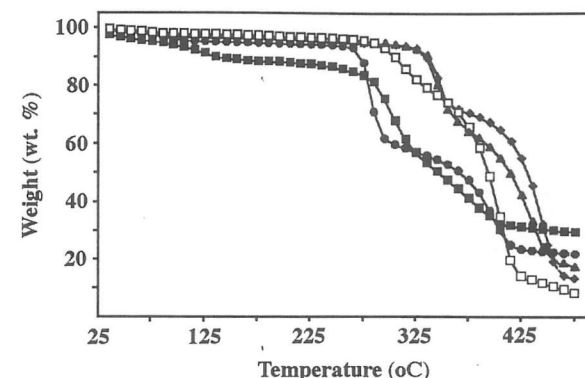


Fig. 4. - thermogravimetric analysis of electrolyte samples (composition n = 5 ■, 30 ●, 50 ▲, 60 ◆, 100 □)

Conclusions

The preparation and characterisation of the behaviour of a lanthanum perchlorate containing polymer electrolyte demonstrates that the modified method for drying the perchlorate salt is applicable to polymer electrolyte synthesis and allows a range of electrolyte compositions to be prepared under conditions which do not require the exposure of thermally unstable perchlorate salts to excessive temperatures.

The fact that commercial PEO contains catalytic residues and thermal and oxidative stabilisers has been commented on by other authors. The exact composition of the commercial sample varies with the supplier and the molecular weight of the polymer produced. This lack of detailed knowledge complicates the interpretation of results obtained, especially under conditions of low salt concentration, as ionic additives may make a significant contribution to the total conductivity. While the repeat unit of PEO contributes to making the macromolecule an excellent solid state solvent, the tendency of the polymer chains to align to form crystalline regions within the material leads to less appropriate behaviour in compositions of low salt content. In applications where optical transparency or optimum conductivity is required these regions of ordered structures are undesirable.

While the current study is of some interest, systems based on other lanthanide ions, which may absorb radiation of an appropriate wavelength to re-emit energy as luminescence, are more likely to find useful technological applications. It has already been shown that europium salts dissolved in polymer hosts have surprisingly long lifetimes in the excited state and narrow bandwidths in the emission spectra [15]. Further studies of the behaviour of luminescent lanthanide salts, perchlorates or anions with a similar degree of hardness/softness, are clearly worth pursuing in order to determine the extent to which materials with different susceptibilities to hydration are a viable basis for the next stage in the development of flexible phosphors. The polymer used in this

study is a convenient model host, however optically more transparent materials, with similar structural attributes, are being prepared for future studies.

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APPLICATION OF THE PITZER THEORY TO THE STUDY OF THE ACETATE pH STANDARD AT 25° C

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Abstract

The mixing parameters, $\theta_{Cl,Ac}$ and $\psi_{Na,Cl,Ac}$, included in the Pitzer equation to evaluate the chloride ion activity coefficient, were determined from electromotive force data, at 25° C. The ionic strength of the mixed electrolyte, sodium chloride and sodium acetate, varied from 0.05 to 2.5 mol kg⁻¹.

The activity coefficient of the chloride ion, in acetate buffer solutions, was calculated using the Pitzer model and the Debye-Hückel theory, with the Bates-Guggenheim convention, and the difference, in pH, has been discussed.

Key words: Acetate buffer solution; Pitzer equations; pH standard

Introduction

The acetate buffer solution has been used as a standard for pH determination. If the procedure for assignment of pH values to the primary standards [1] were applied to this buffer, the difference, in pH, caused by the application of the Pitzer theory instead of the Bates-Guggenheim convention, would be negligible up to ionic strength about 0.4 mol kg⁻¹, as described below.

The assignment of pH to the primary standards involves the calculation of the chloride ion activity coefficient, γ_{Cl} , in the solution at the limit of zero molality of this ion [1], and this calculation is based on the Debye-Hückel theory, using the equation

$$\lg \gamma_{Cl} = A I^{1/2} / (1 + Ba I^{1/2}) \quad (1)$$

where A is the Debye-Hückel parameter, I is the ionic strength and Ba = 1.5, at any temperature, according to the Bates-Guggenheim convention [2]. This is valid for dilute solutions, that is, ionic strength not higher than 0.1 mol kg⁻¹. If the Pitzer theory [3] is applied, the specific ionic interactions are taken into account and γ_{Cl} may be calculated in solutions of higher concentrations, by means of the following equation

$$\ln \gamma_{Cl} = f^{\prime} + 2m_{Na}B_{NaCl} + m_{Na}(2m_{Ac} + 3m_{Cl})C_{NaCl} + m_{Na}m_{Ac}C_{NaAc} + m_{Na}m_{Cl}B'_{NaCl} + m_{Na}m_{Ac}B'_{NaAc} + 2m_{Ac}\theta_{Cl,Ac} + m_{Na}m_{Ac}\psi_{Na,Cl,Ac} + 2m_{HAc}\lambda_{HAc,Cl} \quad (2)$$

$$\lg \gamma_{Cl} = \ln \gamma_{Cl} / 2.303$$

$$f^{\prime} = -A^{\Phi} [I^{1/2} / (1 + bI^{1/2}) + (2/b) \ln(1 + bI^{1/2})] \quad (3)$$

$$B = \beta^{(0)} + \beta^{(1)} (1/\alpha I) [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \quad (4)$$

$$B' = \beta^{(1)} (1/\alpha I^2) [-1 + (1 + \alpha I^{1/2} + (\alpha^2/2)I) \exp(-\alpha I^{1/2})] \quad (5)$$