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CONDUCTIVITY STUDIES OF A POLYMER ELECTROLYTE BASED ON NEODYMIUM TRIFLATE

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Abstract

A new electrolyte prepared from commercial poly(ethylene oxide) and neodymium triflate, in which the salt ions are solubilised by complexation with the oxygen atoms in the polymer structure, has been studied using ac conductivity measurements. The results obtained indicate that the levels of ionic conductivity registered in this system are similar to other multivalent ion based electrolytes. The nature of the charge transporting species in the electrolyte (cations, anions, charged or uncharged ion clusters) cannot be identified with the use of ac techniques and consequently only the total ionic conductivity is reported. The dependence of the ionic conductivity of the electrolyte on the concentration of added salt can however be correlated with the phase behaviour of the polymer - salt system.

Introduction

Solid polymer electrolytes (SPE) films have, for more than a decade, been investigated as candidates for incorporation into a new generation of high performance lithium batteries. Only relatively recently however have fundamental studies been carried out on other multivalent ion based SPEs. As the scientific foundation of these interesting materials accumulates it is becoming increasingly clear that the ion transport processes, the electrode-electrolyte behaviour and the phase structure is rather more complicated than was at first supposed. In this article the conductivity of a trivalent cation containing electrolyte is reported as a function of electrolyte composition and interpreted with reference to an existing partial system phase diagram.

Experimental

Fully hydrated neodymium trifluoromethanesulphonate salt (neodymium triflate) was prepared, as described previously⁽¹⁾, from triflic acid and neodymium carbonate. Prior to use in the preparation of polymer electrolytes the salt was dehydrated at 180°C, under vacuum, for 72 hours. Commercial Poly(ethylene oxide) (Aldrich, PEO mol wt 5×10^6), was dried, under vacuum for one week, at 55 °C. Films of electrolyte were prepared by dissolving the two components in acetonitrile (Aldrich HPLC grade) to form a homogeneous solution which was then transferred to a teflon former located in an isolated evaporating chamber within a preparative argon-filled glovebox. The volume of the electrolyte solution was reduced by slow evaporation to leave a flexible polymer film containing residues of the casting solvent. This film was subjected to a final drying process in an oven at 60 °C under vacuum during a further 48 hours. The composition of the electrolyte produced was controlled by the proportions of polymer and salt in the casting solution and designated by n, the ratio of polymer repeat units to salt ion group (n is therefore the ratio O/M^{3+}). In recognition of the hygroscopic nature of the salt all preparative operations, and the subsequent conductivity experiments, were carried out under a dry argon atmosphere gloveboxes.

Conductivity measurements, by ac technique using a Solartron FRA model 1350 and ECI model 1286 operating between 65 kHz and 0,5 Hz, were applied to films of approximately 150 μm thickness held between gold blocking electrodes (10 mm disks) in a specially designed constant volume cell support⁽²⁾. The electrolyte temperature was monitored by means of a type K thermocouple located close to the film and conductivity measurements were obtained at 5 °C intervals between 25 and 100 °C. The variation of the electrolyte conductivity with temperature was extracted from the complex plane impedance data by non-linear least squares analysis routine using an appropriate equivalent circuit⁽³⁾.

Results and discussion

Since the development of lithium ion conducting SPE's several systems have been studied with the objective of determining the structure of their phase diagrams. It is now widely accepted that these electrolyte systems show fairly complex behaviour with a number of two component

solid-liquid phase regions which form eutectics⁽⁴⁻⁷⁾ over a wide range of composition. Commercial PEO, in common with many other polymeric materials, is a semi-crystalline material. The crystallinity and crystallisation kinetics of the electrolytes formed by addition of salts to the host polymer depend on a variety of factors. On the basis of results reported using multinuclear NMR studies⁽⁸⁾ it is now universally accepted that the ion transport processes occur only in the amorphous fraction of the electrolyte material. While the behaviour of high salt content compositions is of interest from an academic viewpoint, in practical terms the moderate salt content region is of greater importance as it is in this composition range that the electrolyte conductivity is highest. The results of a detailed study of the variation of electrolyte conductivity with temperature and composition can be interpreted with reference to the partial pseudo-equilibrium phase diagram of the system.

In Figure 1 the variation of the total ionic conductivity of several electrolyte compositions with the reciprocal temperature of the electrolyte is shown. Almost all the previously studied electrolyte systems have shown log sigma versus 1/T behaviour which is similarly dependant

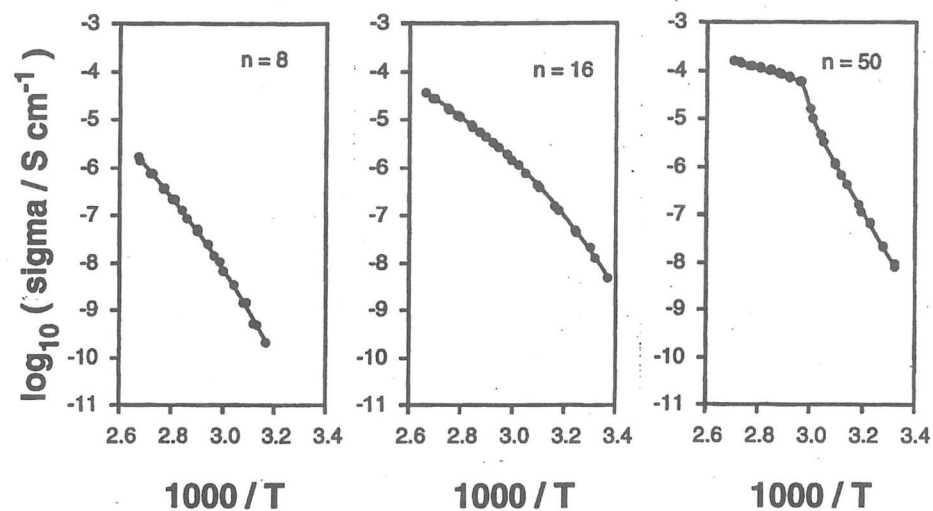


Figure 1 - variation of the total log(conductivity) of electrolyte compositions with 1/T

on the electrolyte composition. In particular the behaviour of the neodymium triflate based electrolyte follows the trends reported for other lanthanum salt containing polymers⁽⁹⁾. Normally at low salt concentrations Arrhenius behaviour is evident with a change of gradient occurring at a temperature close to that of the fusion of the pure PEO spherulites present in the electrolyte. At higher salt concentrations the presence of cations in the electrolyte solution during the deposition process results in "ionic crosslinking" taking place between polymer chains and may retard or even inhibit the formation of pure polymer spherulites. The morphology of the resulting electrolyte film is therefore different and an almost totally amorphous material is formed which shows non-Arrhenius log sigma versus 1/T conductivity behaviour. As reference to Figure 1 demonstrates this type of behaviour is also found with the PEO - neodymium triflate system between the compositions of n = 17 and 7.

Of greater interest is the variation of the total ionic conductivity with temperature and composition, as summarised in the conductivity

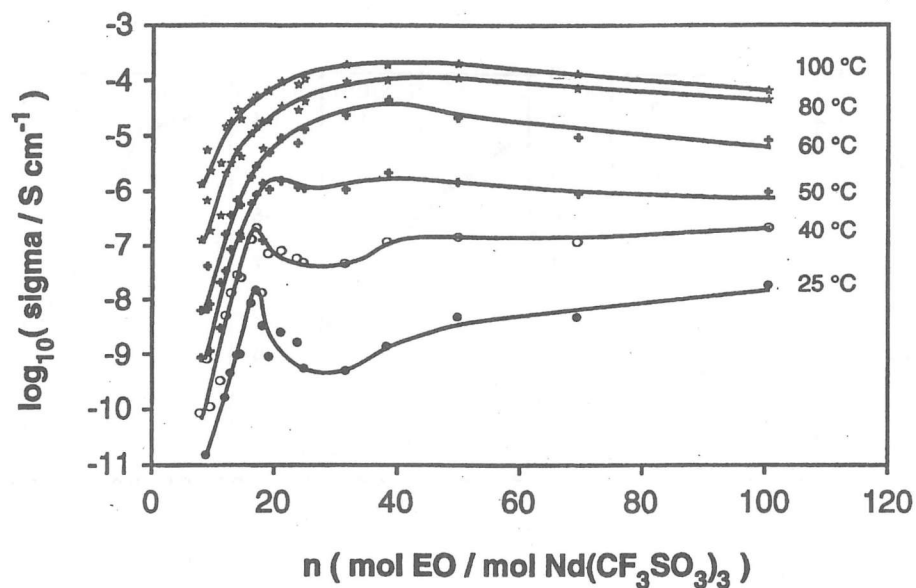


Figure 2 - conductivity isotherms of the neodymium triflate system

isotherms in Figure 2. This figure shows the results of measurements on 19 different electrolyte compositions. At low concentrations of added salt the conductivity of the electrolyte is relatively high and slowly increases with the increase in salt content to a maximum located at close to n = 40. This behaviour is in marked contrast to that reported, in a less complete study of the same system, by other authors⁽¹⁰⁾. It is likely that the difference in the results reported is at least partly due to the difference in hydration state of the salts used though probably the use of other casting solvents also contributes significantly. In certain systems the maximum in electrolyte conductivity coincides with the composition of the eutectic in the system phase diagram. The neodymium triflate system this does not appear to follow this type of behaviour as no thermal evidence was found for a eutectic located in the composition range near n = 40. As the salt content of the electrolyte is increased a significant inflection in the conductivity data is found at n = 15, a value located close to the composition of the phase diagram eutectic. At salt contents between n = 14 and 7 an alteration in the morphology of the material occurs and a decrease in the total ionic conductivity is observed, as expected from the immobilisation of the polymer chains which results from the ionic crosslinking. Recently it has been suggested that the observed conductivity decrease at high salt concentrations may also be caused by the tendency for ion pairs to form⁽¹¹⁾. The relatively low dielectric constant of polyethers favours an extensive ion-ion interaction and naturally an increase in this effect will further reduce the electrolyte conductivity. Raman scattering studies of related polymer electrolytes based on neodymium triflate have demonstrated that extensive ion pairing does indeed occur under certain experimental conditions⁽¹²⁾. The results of these experiments, and the conclusions which may be drawn from them, will be described elsewhere. At still higher concentrations of salt a phase separation of the electrolyte begins and surprisingly a slight increase in electrolyte conductivity is registered. This effect may be due to the onset of phase separation resulting in a decrease in the real concentration of the salt in the amorphous conducting phase. Under these circumstances the conductivity of the material may improve, in spite of the perturbing effect of pure salt crystallites.

Conclusions

Moderate levels of total ionic conductivity have been registered in an polymer electrolyte based on a neodymium triflate system. While the conducting species has not been identified it is probable that this material is predominantly an anionic conductor. At this time it seems unlikely that the electrochemical methods which have been applied successfully to other polymer electrolytes can be used to determine the nature of the charge carrying species in this system.

One of the features of particular interest in this electrolyte is that as the salt concentration is increased the nature of the material becomes increasingly amorphous. While this might be expected to increase the electrolyte conductivity in fact at concentrations of n between 15 and 7 the polymer chain flexibility is reduced to such an extent (or alternatively the ion pair formation is increased) that the level of total ionic conductivity is relatively low and consequently of little commercial interest in many of the possible applications of conventional polymer electrolytes.

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