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Electrical conductivity relaxation in PVOH–LiClO$_4$–Al$_2$O$_3$

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Abstract

We report on electrical conductivity relaxation measurements of solid polymer electrolytes (SPE) based on poly(vinyl alcohol) (PVOH) and LiClO$_4$ in which nanoporous Al$_2$O$_3$ particles with average pore diameter of 58 Å were dispersed. A power law frequency dependence of the real part of the electrical conductivity is observed as a function of temperature and composition. This behaviour is typical of systems in which correlated ionic motions in the SPE bulk material are responsible for ionic conductivity. This variation is well fitted to a Jonscher expression $\sigma'(\omega) = \sigma_0[1 + (\omega/\omega_0)^p]$ where σ_0 is the dc conductivity, ω_0 the characteristic angular frequency relaxation and p is the fractional exponent between 0 and 1. For a prototype membrane with composition 0.9PVOH − 0.1LiClO$_4$ + 7 wt.%Al$_2$O$_3$, it was found that the temperature dependence of σ_0 and ω_0, may be described by the VTF relationship, $\phi = \phi_0 \exp[-B/(T - T_0)]$, with approximately the same constant B and reference temperature T_0, indicating that ion mobility is coupled to the motions of the polymer chains. Moreover, p decreased with increasing temperature, from 0.68 at $T = 319$ K, to 0.4 at $T = 437$ K, indicating weaker correlation effects among mobile ions when the temperature is increased.
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1. Introduction

Much current research in solid sate ionics deals with polymer electrolytes because of their technological importance as thin films in electronic, biomedical and energy-storage devices. A distinguish feature of solvent-free polymer membranes, typically based on amorphous forms of poly(ethylene oxide) (PEO), is that the ion transport includes besides ion motion, local motion of polymer segments and inter- and intrapolymer transitions between coordinating sites formed by the adjacent polyether oxygens [1]. Within such systems lithium salts LiX (e.g. LiBF$_4$, LiClO$_4$, Li(CF3SO$_2$)$_2$N) have shown better performance concerning ionic conductivity at least at high temperature. The addition of inorganic fillers (e.g., Al$_2$O$_3$ nanoparticles) to lithium polymer electrolytes to improve both mechanical and electrical properties has raised great interest [2–6]. It has been reported [3] that decrease of the filler size from micron-scale to nanometer-scale yields a significant increase of the surface-to-volume ratio and enhanced conductivity. Mechanism of such conductivity enhancement has also been studied by using impedance spectroscopy and NMR measurements [4–6]. However, the details of the mechanisms have still been unclear.

In the present work, poly(vinyl alcohol) (PVOH) was selected as a polymer matrix in view of its film-forming capacities, hydrophilic properties and possible coupling of charge transport with the motions of its hydroxyl group [7,8]. Several papers [9,10] reported anhydrous conductivity in the range of 10^{-8} to 10^{-4} S/cm for the lithium salts complexed with PVOH. This contribution therefore focus on ionic conduction behaviour of the PVOH–LiClO$_4$ polymer electrolyte system in which nanoporous Al$_2$O$_3$ particles were dispersed with the objective of looking at their influence on the dynamics of the mobile ions. We used the impedance spectroscopy technique to study the ac electrical response of the studied SPE system in order to study the correlations of structure–conductivity mechanism [11–15]. As demonstrated previously [14–16], the complete characterization of the ac electrical response may be achieved by a detailed

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study of the real part of the conductivity, including the determination of the exact bulk dc conductivity without any use of equivalent circuit analysis.

2. Experimental method

We used 97% hydrolyzed PVOH (Aldrich), average M_W 50,000–85,000 and LiClO$_4$ (Aldrich), which were previously dried under vacuum at 373 K for 5 h. The appropriate quantity of PVOH was poured in deionised water at 353 K. The mixture was put on a stirrer and heated continuously up to 353 K. After 30 min at this temperature, the heater was turned off and a suitable volume of concentrated LiClO$_4$ aqueous solution was poured in the highly viscous PVOH-aqueous solution and stirred for 5 h. Afterwards the mixture was poured into Teflon vessels, under a dry atmosphere, for evaporation of solvent and film membrane formation. We prepare nine concentrations with the weight ratio (x) of LiClO$_4$ to PVOH ($0.02 \leq x \leq 0.3$). We obtained smooth, semitransparent to the visible light, dry to the touch and thin (between 0.05 and 0.20 mm thickness) membranes with good mechanical properties.

Preparation of the composite solid polymer electrolytes (SPE) based on PVOH, LiClO4 and Al$_2$O$_3$ was carried out by adding nanoporous Al$_2$O$_3$ particles with average pore diameter of 58 Å to the PVOH–LiClO$_4$ viscous solutions prepared as described above and stirring continued for 5 h. The added amount was determined from the desired ratio of the inorganic fillers to PVOH–LiClO$_4$ and varied in the range of 2–10 wt.% alumina in SPE. The aspect of membranes with alumina showed a translucent white coloration and they were stronger mechanically.

The electrical properties of the SPEs were determined by admittance measurements using a two-electrode configuration ss|sample|ss (ss: stainless steel, parallel-plate cell) and a home-built temperature and atmosphere controlled cell for measurements. The electrode–electrolyte contact surface (A) and the distance between electrodes (d) were measured using a micrometer. No corrections for thermal expansion of the cell were carried out. Ambient temperature measurements were performed with a HP 4192 A Impedance Analyzer. The admittance response of the membranes was collected by sweeping the frequencies from 5 Hz to 13 MHz with a 100 mV signal. The temperature was measured using a type-K thermocouple placed as close as possible to the cell. As the water content of the membranes is an important parameter, the electrical measurements were done in a shielded cell under a controlled N$_2$ atmosphere, after treating the sample at 383 K in vacuum for 2 h. The weight loss from apparent water content in thermally treated samples did not exceed 0.8 wt.%, as shown by thermogravimetric analysis (TGA) performed with a TA Instruments 2050 microbalance.

From the admittance data, $Y(\omega) = Z(\omega)^{-1} = G_p(\omega) + i\omega C_p(\omega)$ (where $\omega = 2\pi\nu$/Hz is the angular frequency, $i = \sqrt{-1}$ G_p and C_p, the parallel conductance and capacitance, respectively), the real part of the electrical conductivity, $\sigma'(\omega) = (d/A)G_p(\omega)$, was obtained. It is important to stress that $\sigma = (d/A)Y(\omega) = \sigma'(\omega) + i\sigma''(\omega)$ is the preferred quantity to represent the behavior of conducting materials [11–16].
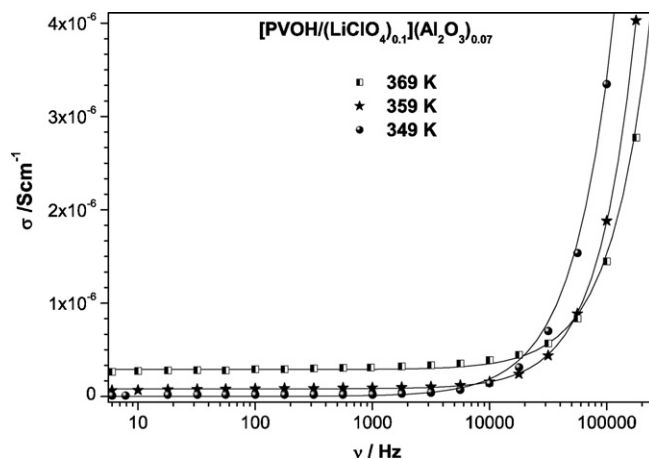

Fig. 1. Frequency dependence of the real part of the conductivity, $\sigma'(\omega)$ vs. log ν(Hz), at several temperatures (from 369 to 349 K) from top to bottom for an alumina doping membrane with composition 0.9PVOH–0.1LiClO$_3$ + 7 wt.%Al$_2$O$_3$. The continuous lines are present calculation using Eq. (1) from 5 Hz to 200 kHz.

3. Results and discussion

Fig. 1 is a typical plot of isotherms of the real part of the conductivity,σ' versus log ν (Hz) for a representative polymer membrane (LiClO$_4$ in PVOH, $x = 0.1$, with Al$_2$O$_3$ content $y = 0.07$) of the studied composites. At frequencies higher than 5 Hz, σ' shows a medium-frequency plateau which corresponds to the bulk dc conductivity of the SPE material, $\sigma_0(T)$ [14–16]. As temperature T is increased the values $\sigma_0(T)$ increase. For a fixed temperature, $\sigma'(T)$ increases with increasing frequency after a characteristic crossover frequency, ν_0, whose values were determined from the data analysis as discussed below, see Fig. 3. These profiles are in accordance with previous studies on other SPEs [13–15] in which an additional low frequency dispersive region is usually observed that is attributed to the electrode–sample interface polarization. It is important to point out that, because of the operational frequency of our instrumentation (from 5 Hz to 13 MHz), it was selected those frequency and temperature ranges and polymer–salt compositions in which both long range transport conductivity (non-dispersive behavior, σ_0) and mobile ion relaxation $\sigma'(\omega) \sim \omega^p$ are present.

The conductivity σ' caused by ionic displacements (hops) are higher at high frequencies than at low ones, because more ionic hops are seen per unit time when the experimental time window, ν^{-1}, is short than when it is long. Thus, σ' is found to be frequency independent in the low frequency region ($\nu < \nu_0$) because the ion diffusion is more correlated, i.e., the ions perform correlated forward–backward motions [11–13]. This relaxation process is fast at high temperatures, but slow at low temperatures. As a consequence, the crossover frequency, ν_0, at which the conductivity attains is dc plateau is found to decrease with decreasing temperature, see Fig. 1.

Conductivity spectra of ion-conducting materials, taken at a fixed temperature, are often found to increase at high frequencies according to a power law, $\sigma'(\omega) \sim \omega^p$, where p is a fractional exponent between 0 and 1. The parameter p has been proposed to be close to 1 for strongly correlated ion motion and equals to