Studies of Ion-Transport Mechanisms in PEM Based on PVA + H₃PO₂ + H₂O

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Abstract: The ionic conductivity for proton exchange membranes (PEM), based on the PVA + H₃PO₂ + H₂O polymer system was studied as a function of temperature. The dc-conductivity of all compositions increases rapidly with the acid concentration, between 10⁻³ and 10⁻¹ S·cm⁻¹ as the acid concentration was increased. Hydrated membranes showed an Arrhenius-type behavior in their conductivities, with an activation energy between 0.20 and 0.10 eV as the acid concentration was increased. When the relative humidity varies between 25% and 92% at room temperature, water uptake increases dc-ionic conductivity varying between 10⁻³ and 10⁻² S·cm⁻¹ for the best performing composition (P/OH = 0.3). The plot of the conductance of the polymer electrolyte as a function of % RH follows a sigmoidal trend. This functional variation was found to be strictly correlated with a similar trend of the film capacitance through a relationship derived from the Onsager equation for liquid electrolytes. Thus, the results support the presence of a (H₃PO₂/H₂O) separated liquid phase in the polymer.

Key words: Proton exchange, dc-ionic conductivity, fuel cell, swollen polymer electrolyte.

1. Introduction

Highly ionic conducting solid polymeric electrolytes have been the focus of research for decades, because its great importance in the development of electrochemical devices such as lithium ion batteries, fuel cells, humidity sensors, among others [1, 2]. Flexible properties of polymeric hosts facilitate the manufacture of thin membrane separating electrolyte in electrochemical devices, making it possible to improve the energy density and achieve high packing.

A polymer electrolyte results from the coordination of a salt with a polymer or when they are dissolved in the presence of cations donors such as acids [2]. When a polymer matrix is coordinated or complexes with ion

donors, charge transport is linked to the mobility of polymeric chains. Otherwise, polymer acts as a host for the electrolyte in aqueous solution as a separate phase such that ionic conductivity is determined by the amount of electrolyte in the matrix. In these water swollen membranes, the conductivity is not directly linked to the polymer dynamics which can be seen in that the conductivity can be high also below the glass transition temperature (T_g) of the polymer, and the temperature dependence of the conductivity can often be described by the Arrhenius equation, $\sigma = \sigma_0 \exp(-E_a/kT)$ [3].

Proton exchange electrolytes made of polyperfluorosulfonic acids such as Nafion® have demonstrated exceptional qualities for application in fuel cells (PEMFC) such as high ionic conductivity (10⁻¹ S·cm⁻¹) when is fully hydrated, good mechanical properties, good thermal stability below 90 °C and high

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chemical inertness [4-7]. However polymeric electrolytes based on PVA have also shown high performance properties for electrolytic applications. Vargas et al. [3], synthesized a high proton conducting ($10^{-1} \text{ S}\cdot\text{cm}^{-1}$) exchange membranes based on PVA, H₃PO₂ and water with good mechanical properties and thermal stability.

In the present work, we focus on additional aspects of the effect of the water content in the PVAL/H₃PO₂ (host) blend on its ion transport mechanism while preserving the dimensional stability of the membranes.

2. Experiments

2.1 Sample Preparation

We used 98%-99% hydrolyzed PVA (Aldrich), with molecular weight ranged between 85.000 and 146.000, and H₃PO₂ in aqueous solution 50 wt.% (Aldrich) as chemicals precursors.

The PVA was poured in deionized water and the mixture was put on a heater-stirrer for 1 h at 120 °C. Once the polymer dissolved the heater was turned off and adequate volume of H₃PO₂-aqueous solution was poured into the PVA-aqueous solution. When this mixture reached ambient temperature (20 °C), it was poured into glass molds, under a dry hood. The samples took several days to become solid. We prepared six H₃PO₂/PVA concentrations, P/OH: 0.10, 0.30, 0.50, 0.75, 1.5, 2.25 and 3.0.

We obtained smooth, uniform, transparent to the visible light and thin (between 0.1 and 0.7 mm thickness) membranes with good mechanical properties. A set of membranes were thermally treated at 100 °C under dry purge air for 10 min.

2.2 Electrical Impedance Measurements

The electrical properties of the membranes were analyzed using impedance spectroscopy. The impedance spectra were taken in the frequency range from 20 Hz to 5 MHz, using a LCR meter (Wayne Kerr 6420) controlled by a computer at an excitation signal of 500 mV. Possible nonlinear effects

were checked at amplitude up to 1.0 V over the entire frequency range for a typical cell of two-electrodes configuration, Pt/membrane/Pt. No significant differences in the impedance spectra were observed. The measuring cell was located in a sealed, temperature and relative humidity controlled home-made chamber. A K-type thermocouple located close to the PVA polymer membrane was used for temperature measurement. The relative humidity in the chamber was measured using an Omega-60 sensor.

3. Results and Discussion

Impedance spectra were represented in Nyquist plots. Fig. 1 shows typical (ReZ, -ImZ) plot taken at 30 and 150 °C for sample P/OH: 0.10 (the inset shows the spectra at 150 °C on an amplified scale). Two well defined regions are shown at low temperature: an arc passing through the origin in the high-frequency limit, which is related to conduction process in the bulk of the sample, and a monotonically decreasing curve with increasing frequency in the low-frequency limit that is attributed to electrode/solid electrolyte interface. Bulk electrolyte resistance coincides with transition between ionic conduction process and diffusion phenomena at the interface. As temperature and acid concentration increase, the low-frequency tail attributed to the sample/electrode interface becomes larger within the operating frequency range and the electrolyte resistance decreases.

Fig. 1 Nyquist plots for the impedance spectra of sample P/OH: 0.10 taken at 30 °C. The inset shows the spectra recorded at 150 °C.

Fig. 2 presents typical spectra of the real part of conductivity, σ vs. frequency (f), for the membrane P/OH: 0.10 at various isotherms. In these diagrams, a well developed non-dispersive intermediate region ("plateau") associated to long-range conduction in the sample volume (dc conductivity) is observed. The dc conductivity (σ_{DC}) at various isotherms was obtained by extrapolating the intermediate flat region to the σ axis (Fig. 2) [8]. As temperature T is increased, the value $\sigma_{DC}(T)$ increases. The profiles observed in the frequency dependence of σ are similar to those observed in other material with disordered structure.

Fig. 3 shows the temperature dependence of $\sigma_{DC}(T)$ for the raw samples in the blend compositions prepared. Based on least square analysis of the corresponding data, straight lines fit well all Arrhenius plots, $\log \sigma_{DC}$ vs. T^{-1} , if a low temperature segment of each data plot is selected (the point is at about 70 °C for samples P/OH: 0.30, 0.50, 0.75 and 1.50, at about 80 °C for sample P/OH: 2.25, and 100 °C for sample P/OH: 3.00). For P/OH: 0.1, there is no a definite trend. Upper limit of each range marks the onset temperature at which water content into the membranes are no longer at equilibrium with the surrounding atmosphere and starts to diffuse out the membrane, leading to a decrease in conductivity [3, 9].

Fig. 4 shows the Arrhenius plots of the dc conductivity data for thermally treated samples in which three linear trends are observed. In the first region, between 30 and 90 °C, the data could be fitted with straight lines over the entire range because the effect of water loss was not significant. In the second region, between 100 and 130 °C, ionic conductivity has a lower thermal activation and linear fittings could be made up to 130 °C where divergences from the linear behavior are observed above 130 °C (third region), which is probably due to softening of the PVA matrix.

Table 1 gives the activation energy (E_a) calculated from the fitting parameter according to the Arrhenius model, $\ln \sigma_{DC} = \ln \sigma_o + E_a/kT$. Note that E_a decreases

slightly with increasing acid concentration for raw samples, e.g., from 0.14 to 0.10 eV. For heat treated samples, they show slightly different activation

Fig. 2 Dependence of ionic conductivity with frequency P/OH: 0.10.

Fig. 3 Logdc-conductivity vs inverse temperature plots for raw samples. Solid lines are linear fittings to the Arrhenius model $\ln \sigma_{DC} = \ln \sigma_o + E_a/kT$.

Fig. 4 Logdc-conductivity vs inverse temperature plots for heat treated samples. Solid lines are linear fittings to the Arrhenius model $\ln \sigma_{DC} = \ln \sigma_o + E_a/kT$.

Table 1 Arrhenius activation energy, E_a , for the raw and heat treated samples, calculated from the linear fitting to the Arrhenius model.

P/OH	E_a (eV)		
	Raw samples	Heat-treated samples Region I	Region II
0.10	0.37	0.31	0.09
0.30	0.20	0.14	0.04
0.50	0.13	0.14	0.04
0.75	0.14	0.13	0.05
1.50	0.11	0.11	0.06
2.25	0.10	0.11	0.04
3.00	0.10	0.14	0.11

energies comparable with those shown by the raw samples, but they did not show the same trend as a function of the acid content. In region II the abrupt decrease of the activation energy, indicates that the conduction process is less sensitive to increases in temperatures above 100 °C.

Previous work has shown that when the system PVA/H₃PO₂/H₂O is subject to more severe dehydration processes, the Arrhenius plots of the dc-conductivity data is better described by the Vogel-Tammann-Fulcher (VTF) model [3, 9, 10] in the whole temperature range studied. This indicates that when this system is dehydrated, the processes that contribute mostly to the overall dc-conductivity of the anhydrous membranes are mainly regulated by the segmental motions of the polymer chains.

The dependence of conductivity on acid concentration, P/OH, is presented in Fig. 5, in which $\log \sigma$ vs P/OH is plotted for raw and heat-treated samples at 30, 60 and 100 °C isotherms. It is quite evident that the dc-conductivity initially increases rapidly with increasing acid content up to about P/OH: 0.30. Previous studies on the system have shown that the amount of water absorbed by the membranes increases with acid concentration [10]. The results then indicate that the proton transport properties of the membranes with high acid concentrations are both directly linked to a two-phase structure, where liquid-like H₃PO₂/H₂O clusters expand with increasing acid content, and the membranes become more

proton-conducting whereas the solid-like polymer backbone maintains the mechanical stability. For heat treated sample, the dc conductivity is slightly lower than those for the raw samples (except for the 30 °C isotherm), due to less water content, but the composition dependence of conductivity is similar.

Fig. 6 shows the dependence of the dc conductivity of the membrane P/OH: 0.30 on the relative humidity of the surrounding atmosphere, RH%. Due to the hydrophilic character of the membranes, the dehydration process is reversible, and the conductivity improvement upon increasing RH% is attributed to the proton transport in a liquid phase H₃PO₂/H₂O as previously proposed [3, 10]. On the basis of modified Onsager model [11], we may describe conductivity

Fig. 5 Logdc-conductivity vs concentration for 30, 60 and 100 °C isotherms.

Fig. 6 Dependence of dc-conductivity with environment relative humidity for the system P/OH: 0.30.

Table 2 Sigmoidal parameters for the fitting of the dc conductivity data as function RH%.

	Value	Error
A_1	1.43E-03	1.10E-04
A_2	1.78E-02	1.46E-04
x_0	65.67311	0.37708
dx	6.35274	0.31271

dependence with RH%. This model considers that the ions can dissolve in the polymer liquid phase and its polar character, which is function of the absorbed water, is responsible for solvation that shields the Coulomb interaction among the ionic species.

The solid line in Fig. 6 represents the sigmoidal fitting (Eq. 1) to the humidity (RH%) dependence of the dc-conductivity:

$$y = A_2 + \frac{A_1 - A_2}{1 + \exp \frac{(x-x_0)}{dx}} \quad (1)$$

where, A_1 represents the lowest conductivity value, A_2 the asymptotic limit of the conductivity at highest RH%, $(x-x_0)$ the relative humidity range in which the fitting is done and dx is a fitting parameter. Table 2 gives the best fitting parameters to Eq. (1).

Starting from the A_2 parameter, it is possible to build the Onsager model fit (for example Ref. [12] for the polymer/salt complex FeCl₃-doped polypropargylalcohol (F-POHP)); however, in our case, it was not possible to apply the Onsager equation to the conductivity data for the membrane PVA/H₃PO₂/H₂O, because the dielectric constant of the liquid like phase clusters into the membranes was not determined. However, the sigmoidal trend observed for the plots σ versus RH% of the PVA/H₃PO₂/H₂O membranes (Fig. 6) are similar to that reported in Ref. [12] following the same sigmoidal trend. This finding supports the presence of a (H₃PO₂/H₂O) separated liquid phase created in the polymer due to water absorption.

4. Conclusions

The variation of the electrical conductivity of PVA/H₃PO₂/H₂O membranes with temperature, acid concentration and environment relative humidity was studied. The membranes reached high ionic

conductivities of the order of 10⁻¹ S·cm⁻¹ at room temperature for high acid concentrations. The dependence of dc-ionic conductivity with temperature and environmental relative humidity (RH%), confirmed the hypothesis of the presence of two separate phases in this system: a solid phase with constant composition (PVA/H₃PO₂) and a liquid phase (H₃PO₂/H₂O) with variable composition, primarily responsible for the ion migration in the blend for low acid concentration.

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