THERMOELECTRIC STUDIES OF THE POLYMER ELECTROLYTE POLY(VINYL ALCOHOL) - AGI –H_2O

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Abstract

In this work we used impedance spectroscopy (IS) and differential scanning calorimetry (DSC) techniques to study the polymer electrolyte poly(vinyl alcohol) - AgI –H_2O. AgI and PVAL (Al-drich) were used to prepare the system with the salt/polymer mass fraction: x=0.096. We got membranes with thicknesses of 0.2 mm. The impedance spectroscopy studies were obtained from Hz to 10^9 Hz over the temperature range 22 to 65°C. The polymer electrolyte exhibited an ionic conductivity of the order 10^{-3} Scm^{-1} at room temperature for the hydrated samples. The permittivity curves reveal two dielectric relaxations at around 10^6 and 10^9 Hz. The DSC results show for dry samples that the glass transition phase is no sensible to the AgI content and appears at around 75 ^oC. Two more phase transitions appear at about 150 and 200 ^oC corresponding to the superionic silver phase transition and the PVAL melting point, respectively

keywords: *Solid Polymer electrolyte, PVAL, AgI, Ionic conductivity, Phase transition.*

Resumen

En este trabajo usamos técnicas de espectroscopia de impedancias (IS) y calorimetría de barrido diferencial (DSC) para el estudio del polímero electrolito poly(vinyl alcohol) – AgI- H_2O. El AgI y el PVAL (Al-drich) fueron usados para preparar el sistema con fracción de masa sal/polímero x=0,096, obteniendo membranas con espesores de 0,2 mm. Los estudios de espectroscopia de impedancias fueron obtenidos desde los Hz hasta 10^9 Hz y en un rango de temperatura de 22 a 65^oC. El polímero electrolito muestra una conductividad iónica del orden de 10^{-3} Scm^{-1} a bajas temperaturas para la muestra hidratada. En los resultados de DSC se observa, para las muestras secas, que la transición de fase vítrea no es sensible a la adición del AgI y aparece alrededor de 75^oC, se observan otras dos transiciones de fase alrededor de 150 y 200 ^oC correspondientes a la transición de fase superiónica de la plata y al punto de fusión del PVAL respectivamente.

Palabras calve*:Electrolíto de polimero sólido, PVAL, AgI, Conductividad iónica, Transición de fase.*

INTRODUCTION

Polymer electrolytes have been the focus of intense research efforts due to their potential application in rechargeable batteries and electrochemical sensors (Gray [1], Armand [2]). These membranes consist of a polymer matrix swollen with water and electrolyte solutions such as the systems of poly(vinyl alcohol) (PVAL) with different salts, which have received considerable attention since they exhibit solid phases with high ionic conductivity at room temperature. These systems combine the mechanical properties of the solid polymer electrolytes with the high ionic conductivity of liquid electrolytes. The high conductivity is assigned to the amorphous phase of the polymeric matrix, assisted by the segmental motion of the polymeric backbone. A limited number of silver ion conducting polymers have been studied, but some of the reported ones indicate relatively high conductivities (Sreepathi *et al* [3], Eliasson *et al* [4]). It is also common to find relaxation phenomena in polymers (Eliasson *et al* [4]).

In this work we study solid polymer electrolyte membranes consisting of PVAL, AgI and water. These membranes have been prepared and characterized by thermal and electrical

measurements. These samples show dielectric relaxations, good stability and high ionic conductivity.

1. EXPERIMENTAL METHODS

(AgI) and (PVAL) were used to prepare the system (PVAL) – (4AgI) – H_2O, with the following salt/polymer mass fraction: x = 0.096, we got uniform and smooth polymeric membranes with thicknesses of 0.2 mm.

The thermal characterization was carried out by using a DSC 30 calorimeter controlled by a microcomputer at a temperature rate of 10 °C/min. The measurements were done under a nitrogen atmosphere.

Complex impedance measurements were performed on disc-shaped polymer electrolyte samples sandwiched between two stainless-steel electrodes of 5 mm diameter, using a HP 4291A RF impedance analyser in the 1 MHz–1.8 GHz high-frequency range from 10 to 65 °C. The temperature of the sample was controlled using a thermostatic bath and measured with a chromel–alumel thermocouple.

The dc-conductivity, σ_o, was determined from the R_{bulk} values obtained from the impedance plots. The real and imaginary part of the complex permittivity were determined from the impedance data, $Z=Z'-iZ''$, using $C= -1/\omega Z''$ and $\varepsilon=C/C_o$ where C is the capacitance of the measuring cell and C_o the geometric capacitance of empty sample cell.

2. RESULTS AND DISCUSSION

Figure 1 shows the DSC curve for PVAL-AgI-H_2O (salt/polymer mass fraction x=0.096) using a heating rate of 10 ^oC/min with a dry N_2 flux. The DSC resuls for a dry samplet show three anomalies for PVAL-AgI-H_2O , the first one as a step around 75 °C associated to the glass transition (Tg), the second one as an endothermic peak around 150 °C corresponding to the superionic silver phase transition and third one as an endothermic peack around 200 ^oC associated to the melting point of the PVAL. We can observe that the glass transition phase is no sensible to the AgI addition as it is for other compounds (Palacios *et al* [5],Vargas *et al* [6], Fernández *et al* [7]).

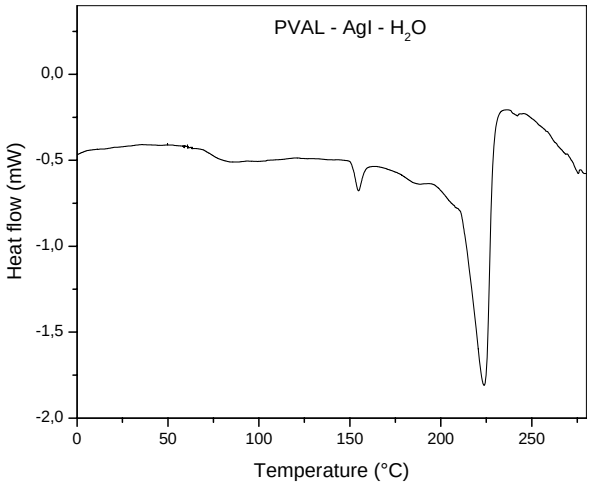


Figure. 1. DSC curve for PVAL-AgI-H2O (salt/polymer mass fraction x=0.096) using a heating rate of 10 ^oC/min with a dry N_2 flux.

Figure 2 shows the *dc*-conductivity vs. reciprocal temperature of (PVAL) – (AgI) – H_2O between 22 and 65 ^oC during a heating run. The hydrated

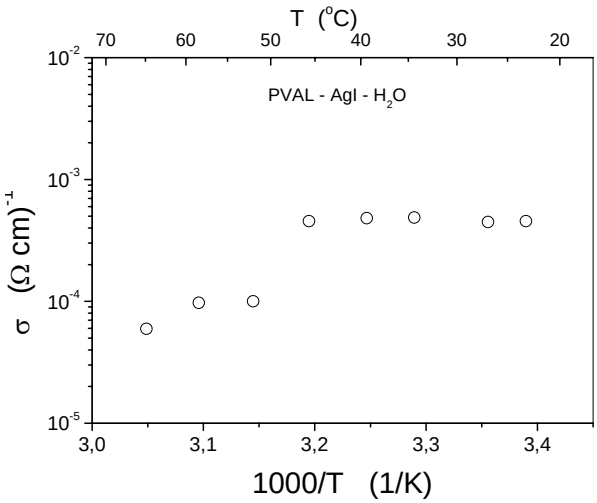


Figure 2. dc-conductivity vs. reciprocal temperature of (PVAL) – (AgI) – H_2O between 22 and 65 ^oC

polymer electrolyte exhibited an ionic conductivity of ~ 10^{-3} Scm^{-1} at room temperature and still constant until around 50 ^oC, after this temperature it decreases as the temperature increases due to the water weight loss.

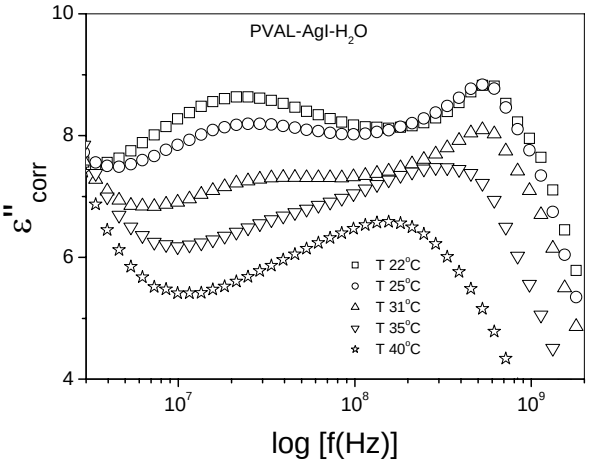


Figure. 3 The imaginary parts, ε´´, of the dielectric permittivity for PVAL–AgI–H_2O over the available frequency range.

The imaginary part of the permittivity after subtracting the *dc*-conductivity contribution, ε_c"(ω,T), as a function of frequency at several isotherms (T≤ 40 °C) is shown in Figure 3 for (PVAL) – (AgI) – H_2O. Two broad peaks are observed at high frequencies, for example, at 22 °C the peak frequencies, f_{max}, are about $2*10^7$ Hz and $5*10^8$ Hz respectively. The relaxation at about $2*10^7$ Hz is due to the water content. As the temperature increases the relaxation intensity decreases until disappear due to the water weight loss. *T*he peak of the second relaxation correlated at $5*10^9$ Hz is not well resolved due to instrument limitation on its frequency operation. We have observed this relaxation in another polymer electrolyte based in PVAL (Fernández *et al* [8])

3. CONCLUSIONS

The hydrated polymer electrolyte exhibited an ionic conductivity of ~ 10^{-3} Scm^{-1} at room temperature and still constant until around 50 °C, after this temperature it decreases as the temperature increases due to the water weight loss. The Impedance spectroscopy results reveal two dielectric relaxations, the first one at about $2*10^7$ Hz due to the water content and the second one at about $5*10^9$ have also been observed in another polymer electrolyte based in PVAL. The DSC results show that the glass transition phase is no sensible to the AgI and appear at around 75 °C, two more phase transitions appear at about 150 and 200 °C corresponding to the superionic silver phase transition and the PVAL melting point, respectively.

4. ACKNOWLEDGEMENTS

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