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A Study On Ionic Conductivity And Thermal Behavior Of Heteropolyacid Impregnated PVDF As A Solid Polymer Electrolyte For Dye-Sensitized Solar Cells

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ABSTRACT

Conductivity and thermal behavior of heteropolyacid (HPA) impregnated poly(vinylidene fluoride) (PVDF) with iodine/iodide was investigated mainly for exploring its use as an electrolyte for dye-sensitized solar cells (DSSC). The prepared polymer electrolyte membranes has been found to be thermally stable and the conductivity measured at room temperature is 2.11 x 10^{-5} S cm^{-1}, which is higher than that of HPA impregnated PVDF without iodine/iodide and I_2/I_3^- doped PVDF without HPA. Further, an increase in conductivity is realized by increasing the temperature and the relative humidity, which has a relevance future in DSSC.

KEYWORDS

Conductivity;
Polymer electrolyte;
Poly(vinylidene fluoride);
Heteropolyacid

INTRODUCTION

The field of solar electricity, or photovoltaics, is rich in that there are many materials and concepts for converting sunlight into electricity. The dye-sensitized solar cell (DSSC), developed in the 1990s[1], is a nonconventional solar electric technology that has attracted much attention, perhaps a result of its record cell efficiency above 10%. The electrolyte loss caused by the leakage and/or volatility of the electrolyte solution has been pointed out to be one of the major problems, which stays the durability of the DSSC low. In this regard, currently extensive efforts have been dedicated to the research and development of new electrolytes for dye-sensitized solar cell applications to attain stable and high efficiency performance[2-7]. In particular, solid polymer electrolytes have attracted considerable attention due to their interesting application potential in solid-state electrochemical devices such as secondary batteries[8], electrochromic displays[9], light emitting electrochemical cells[10], super capacitors[11] and fuel cells[12]. These features have given an impetus to develop suitable electrolytes showing high conductivity and better thermal properties for dye-sensitized solar cells by replacing the known liquid electrolytes(iodine/iodide). Wang et al.[13] recently employed a polymeric gel electrolyte containing 1-methyl-3-propylimidazolium iodide and poly (vinylidene fluoride-co-hexafluoropropylene) to fabricate a DSSC of efficiency 5.3%. Similarly many researchers[14-17] designed a new series of polymer electrolytes for investigating a solid-state version of regenerative dye-sensitized TiO_2 solar cells. In order to understand the phenomenon of enhanced ionic transport and to gain further insight into DSSC, here we report the conductivity and thermal behavior of HPA impregnated PVDF with iodine/iodide based electrolyte for the possibility of using it in DSSC to attain enhanced efficiency.

EXPERIMENTAL

The starting materials used are poly(vinylidene fluoride)(Good Fellow) and heteropoly tungstate (Aldrich). All the other chemicals used are the purest research grade available. A typical synthesis of modified polymer electrolytes was carried out as follows. Doped PVDF-I_2/I_3^- polymer electrolyte (E1) was prepared by the addition of 0.03 and 0.003 g of KI and I_2 to desired amount of PVDF (0.3g) in 25ml of DMF at 80^{0}C. Similarly HPA impregnated PVDF with iodine/iodide(E3) and without iodine/iodide (E2) were prepared by the addition of 0.036 g HPA (less than 1 wt %) to the same amount of PVDF in 25 ml of DMF at 80^{o}C. For characterization studies, thin polymer electrolyte membranes were cast by vacuum evaporation of solvent at 80^{o}C. Thermogravimetry (TGA) analysis of the composite membrane was performed on a PL thermal analysis system (STA 1500 series) in a temperature range from 25 to 650^{o}C at the heating rate of 10^{o}C/min in air. Further, the complex impedance analysis of these thin films was performed using Autolab PGSTAT with FRA module coupled to a computer over the frequency domain 1 MHz to 10 Hz with amplitude of 5mV and in the temperature range 300-373 K with an aid of a pair of gold plates(1cm^2) as electrodes. The conductivity of the membrane was determined from the high frequency intercept of the impedance with the real axis, and was calculated using the following equation: $\sigma = L/RS$, where σ, L, R and S denote the ionic conductivity, thickness of the membrane, the resistance of the membrane and the cross-sectional area of the membrane, respectively. Conductivity measurements at different humidity conditions were performed in the same way mentioned above, but maintaining the samples under controlled humidity conditions (%RH=0, 31, 81 and 100) at 27^{o}C. The thickness of the film used for electrochemical impedance technique is measured by air-wedge technique[18].

RESULTS & DISCUSSION

Figure 1 illustrates a typical AC impedance spectrum for a HPA impregnated PVDF with iodine/iodide (E3) membrane at different temperatures (300, 333, 373 K). Generally for polymer electrolytes, two semicircles should appear in the impedance spectrum i.e., one at higher frequencies corresponding to the bulk electrolyte impedance and the other at lower frequencies related to the interfacial impedance. This is well confirmed by Watanabe and Ogata[19] from their theoretical and practical analysis of "true" solid polymer electrolytes such as poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPO). But, such high frequency semicircle does not appear in practical impedance plots for these polymer electrolytes similar to the plasticized PVDF/HFP and celgard

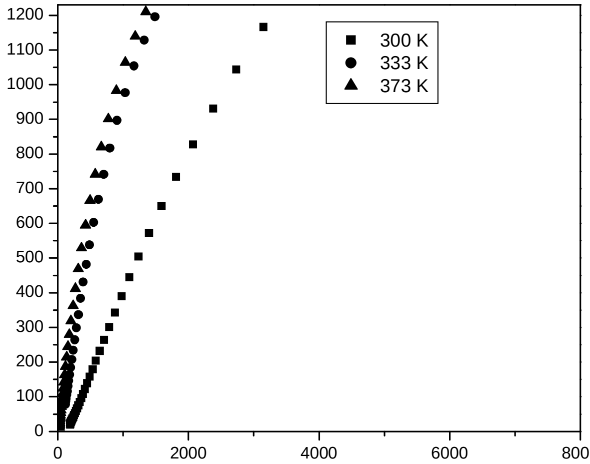

Figure 1 : Typical ac-impedance spectrum for HPA impregnated PVDF with iodine/iodide at three different temperatures (a) 300 K, (b) 333 K, and (c) 373 K

2400 membrane[20,21]. This may be due to the facile ion mobility in liquid- and gel-type electrolyte systems, when compared with solid polymer electrolytes, implies that ions possess small dielectric relaxation times and hence the inconsequential capacitative effect of the bulk electrolyte in the spectrum. Thus, the absence of semicircular portion in the complex impedance plots led to a conclusion that the current carriers are ions and this leads one to further conclude that the total conductivity is mainly the result of ion conduction. Similar trends were observed for other polymer membranes also(I_2/I_3^- doped PVDF(E1), HPA impregnated PVDF without iodine/iodide(E2).

The conductivity of the HPA impregnated PVDF with iodine/iodide (E3) was measured as a function of temperature. The temperature dependence of electrical conductivity(σ) may be expressed by the Arrhenius equation:

$\sigma_{(T)}=\sigma_0 T^{1/2} \exp(-E_a/kT)$

where σ_o is the pre-exponential factor, E_a, the activation energy for ionic migration within the solid, k, the Boltzmann constant and T is the absolute temperature. Figure 2 shows the variation of log(σT) as a function of inverse of absolute temperature for iodine/iodide doped PVDF (E1), HPA impregnated PVDF with iodine/iodide (E3) and without iodine/iodide (E2). As evidenced in figure 2, the conductivity increase by increasing the temperature for all the membranes used in this study and HPA impregnated PVDF with iodine/iodide (E3) shows maximum conductivity compared to the I_2/I_3^- doped PVDF without HPA (E2) and HPA impregnated PVDF without iodine/iodide (E3). According to the data fitting, E_a was determined for all the samples. The values are in agreement with the literature[22], where a value near to 0.1 eV is suggested for most of the polymer electrolytes. The higher activation energy values observed for the composite membranes might be caused by the presence of inorganic additives in the polymer electrolyte.

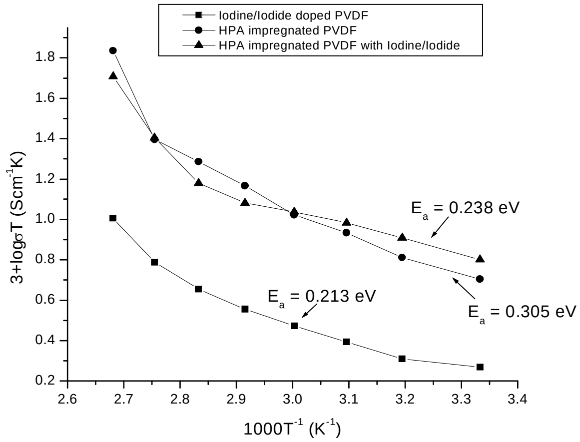

Figure 2 : Arrhenius plot of the ionic conductivity of (a) iodine/iodide doped PVDF (■), (b) HPA impregnated PVDF without iodine/iodide (●), and (c) HPA impregnated PVDF with iodine/iodide (▲)

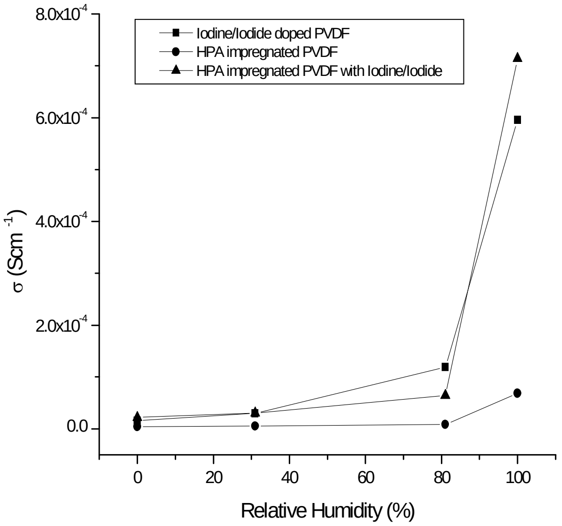

Figure 3 : Variation of ionic conductivity as a function of the relative humidity of(a) iodine/iodide doped PVDF (■), (b) HPA impregnated PVDF without iodine/iodide (•), (c) HPA impregnated PVDF with iodine/iodide (▲)

Ambient humidity adsorbed in the polymer affects its conductivity and is important to analyze this property because the assemblage of solar cells takes place at room temperature and humidity conditions. Hence humidity control studies at room temperature was achieved by keeping the sample above the concentrated salt solutions of $CaCl_2$ in a closed container to produce a relative humidity of 31% and saturated $(NH_4)_2SO_4$ to produce a 81% relative humidity environment[23,24]. To obtain a 100% relative humidity environment, de-ionized water was used and for a 0% relative humidity environment, solid P_2O_5 was placed in the bottom of the chamber. Figure 3 depicts the variation of the ionic conductivity as a function of relative humidity, which describes

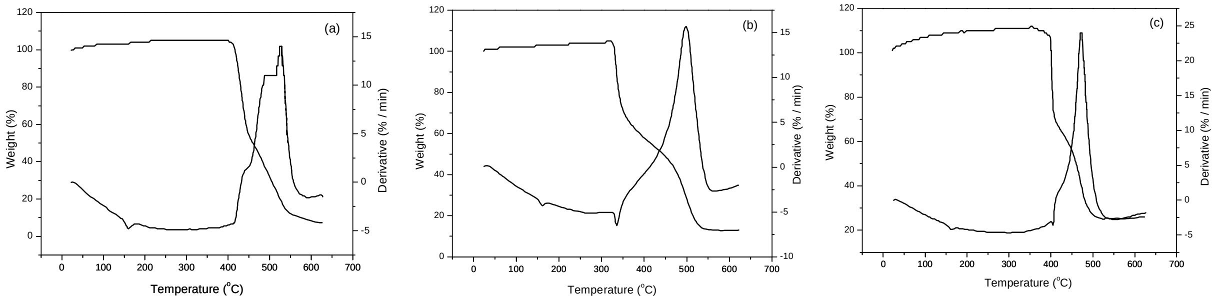

Figure 4 : TGA thermograms and associated derivative curves, taken for (a) iodine/iodide doped PVDF, (b) HPA impregnated PVDF without iodine/iodide, and (c) HPA impregnated PVDF with iodine/iodide

the ionic conductivity increase with humidity. This is an interesting result because it is possible to predict the conductivity of electrolyte used in an electrochemical cell working at known relative humidity conditions.

The thermal behavior of HPA impregnated PVDF with iodine/iodide was investigated to provide a better understanding of the system in view of the observed temperature-dependence of the conductivity. The TGA thermograms of the iodine/iodide doped PVDF (E1) and HPA impregnated PVDF with iodine/iodide (E3) and without iodine/iodide (E2) were displayed in figure 4. From figure 4, it is seen that all the membranes retain more than 95% of their weight up to a temperature of about 300^{o}C. Above 300^{o}C, all the membranes started to decompose in a rapid manner. In order to ensure the above findings in detail, the DTA analysis on the membranes will be more helpful. The melting endotherm corresponding to PVDF is observed at 161±2^{0}C for all the prepared polymer electrolytes. HPA impregnated PVDF with iodine/iodide (E3) and without iodine/iodide (E2) shows endothermic effects at ca. 405 and 326^{o}C, which can be assigned to the removal of crystallization water and the water molecules hydrating protons, respectively due to the added heteropolyacids[25,26]. The exothermic transformation above 450^{o}C on DTA curve of membranes were due to decomposition of polymer and as well as the keggin anion[25-27]. Thus, these polymeric electrolytes exhibit an excellent thermal stability.

From the TGA and impedance analysis, it is concluded that the present system has thermal stability up to 300^{o}C and this allows their use in solid-state photo and electrochemical devices because they operate at temperatures below 120^{0}C. This property is more affected when dealing with solar cells, because the thermal radiation from the sun causes an increase of the operational temperature. The purpose of this study is to develop a polymeric electrolyte with high conductivity and suitable dimensional stability and thermal properties to be applied in photoelectro chemical devices. In order to examine the photovoltaic device performance, preliminary data is submitted here. That is, the current (I)- voltage (V) characteristics of the fabricated solar cells have been measured in the dark and under illumination (area of 1 cm^2 with a tungsten halogen lamp of intensity 15 mW/cm^2) using Solartron 1260 electrochemical measurement unit. For the [FTO/TiO$_2$/dye/E3/Conducting Carbon Cement] cell (where E3 is HPA impregnated PVDF with I_2/I_3^- polymer electrolyte), we observed an open circuit voltage(V_{OC}) of 426 mV, a short circuit current(I_{SC}) of 3.90 mA, and a fill factor (FF) of 0.25.

In summary, a new type of polymer electrolyte was investigated for solar energy conversion processes. The results obtained are very encouraging and further improvement of the photovoltaic performance is expected, as many parameters of the cell assembly and of the electrolyte had not been yet optimized. Also, long-term stability measurements of the cell are in progress.

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