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Structural, vibrational and electrical characterization of PVA–NH_4Br polymer electrolyte system

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Abstract

Polymer electrolyte based on PVA doped with different concentrations of NH_4Br has been prepared by solution casting technique. The complexation of the prepared polymer electrolytes has been studied using X-ray diffraction (XRD) and Fourier transform infra red (FTIR) spectroscopy. The maximum ionic conductivity ($5.7 \times 10^{-4}\,S\,cm^{-1}$) has been obtained for 25 mol% NH_4Br-doped PVA polymer electrolyte. The temperature dependence of ionic conductivity of the prepared polymer electrolytes obeys Arrhenius law. The ionic transference number of mobile ions has been estimated by dc polarization method and the results reveal that the conducting species are predominantly ions. The dielectric behavior of the polymer electrolytes has been analyzed using dielectric permittivity and electric modulus spectra.

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Keywords: Polymer electrolyte; XRD; FTIR; Ionic conductivity; Transference number

1. Introduction

Interest in solid proton-conducting polymer electrolytes started with the development of perfluorinated sulfonic membranes in the 1960s [1]. In recent years, proton-conducting polymer electrolytes have been intensively studied as a perspective material for various electrochemical devices such as fuel cells, sensors, electrochromic displays and electro chromic windows [2]. Few reported proton-conducting polymer electrolytes are complexes of strong inorganic acids (H_3PO_3, H_2SO_4, HCl) or ammonium salts (NH_4SCN, $NH_4CF_3SO_3$, NH_4HSO_4, NH_4ClO_4, $(NH_4)_2SO_4$, NH_4I) with commercially available electrodonor polymers (PEO, PVA, PAA, PEI) [3–10]. However, proton-conducting polymer complexes with inorganic acids suffer from chemical degradation and mechanical integrity making them unsuitable for practical applications.

Considering this fact and due to lack of good proton-conducting polymer electrolyte working at ambient temperatures, search for the new systems has been perused in the past few years. The present work aims at developing a new type of proton-conducting polymer electrolyte with 88% hydrolyzed PVA as the host polymer. It is to be noted that the conductivity is typically higher for 88% hydrolyzed than 99% hydrolyzed PVA [11]. In the present study, NH_4Br has been chosen as the dopant since ammonium salts are considered as the good proton donor to the polymer matrix [12,13]. The prepared polymer electrolytes have been characterized by X-ray diffraction (XRD), Fourier transform infra red (FTIR) and ac impedance spectroscopic techniques.

2. Experimental

Poly(vinyl alcohol) (PVA, M_w: 1,25,000, 88% hydrolyzed, AR grade, s.d. Fine) and NH_4Br (AR grade, s.d. Fine) have been used as the raw materials in this study. To avoid absorption of water, the powdery polymer

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(PVA) and the salt (NH_4Br) are vacuum dried before usage. Appropriate quantities of PVA and NH_4Br in aprotic solvent, DMSO (dried and distilled before usage) are stirred continuously for several hours until a homogenous solution has been obtained. The obtained solution is then casted in glass petri dishes and is subjected to drying (70 °C for 5 days) in a vacuum chamber. Mechanically strong, transparent and flexible films of thickness ranging from 0.2 to 0.4 μm are obtained.

X-ray diffraction patterns have been recorded at room temperature on a Philips X'Pert PRO diffractometer equipped with an X'celerator detector, using the Cu Kα radiation in the range of $2\theta = 5$–90°. The FTIR spectrum has been recorded using Shimadzu 8000 spectrophotometer in the frequency range 400–4000 cm^{-1}. Electrical measurements have been performed on a HIOKI make LCZ meter (model 3532) in the frequency ranging from 42 Hz to 5 MHz at different temperatures from 303 to 343 K using stainless steel blocking electrodes. The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport have been evaluated in PVA–NH_4Br electrolyte system using dc polarization method. The electrical conductivity study has been carried out in a hermetic cell described elsewhere [14].

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1(a and b) represents the XRD pattern of pure PVA and 25 mol% NH_4Br-doped PVA, respectively. A broad peak at 19.7° ascribed to pure PVA [15,16] has been observed in Fig. 1(a). An increase in broadness and a decrease in the intensity of 19.7° peak has been observed in the NH_4Br-doped PVA. This increase in broadness of the peak reveals the amorphous nature of the complexed system. These results can be interpreted in terms of the Hodge et al. [16], criterion which has established a correlation between the height of the peak and the degree of crystallinity. No new peaks have been found in the complex indicating a complete dissociation of salt in the polymer matrix. Thus, the XRD analysis reveals the complex formation in the polymer matrices. The increased amorphous nature of pure PVA doped with 25 mol% NH_4Br has been confirmed from XRD results.

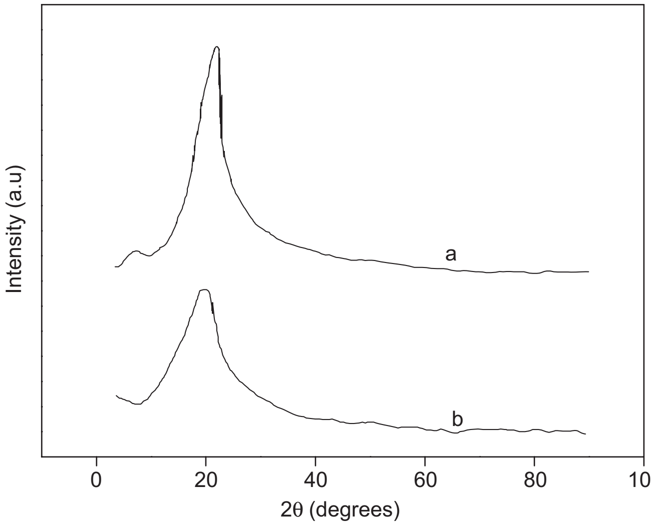

Fig. 1. XRD pattern of (a) pure PVA and (b) 25 mol% NH_4Br-doped PVA polymer electrolytes.

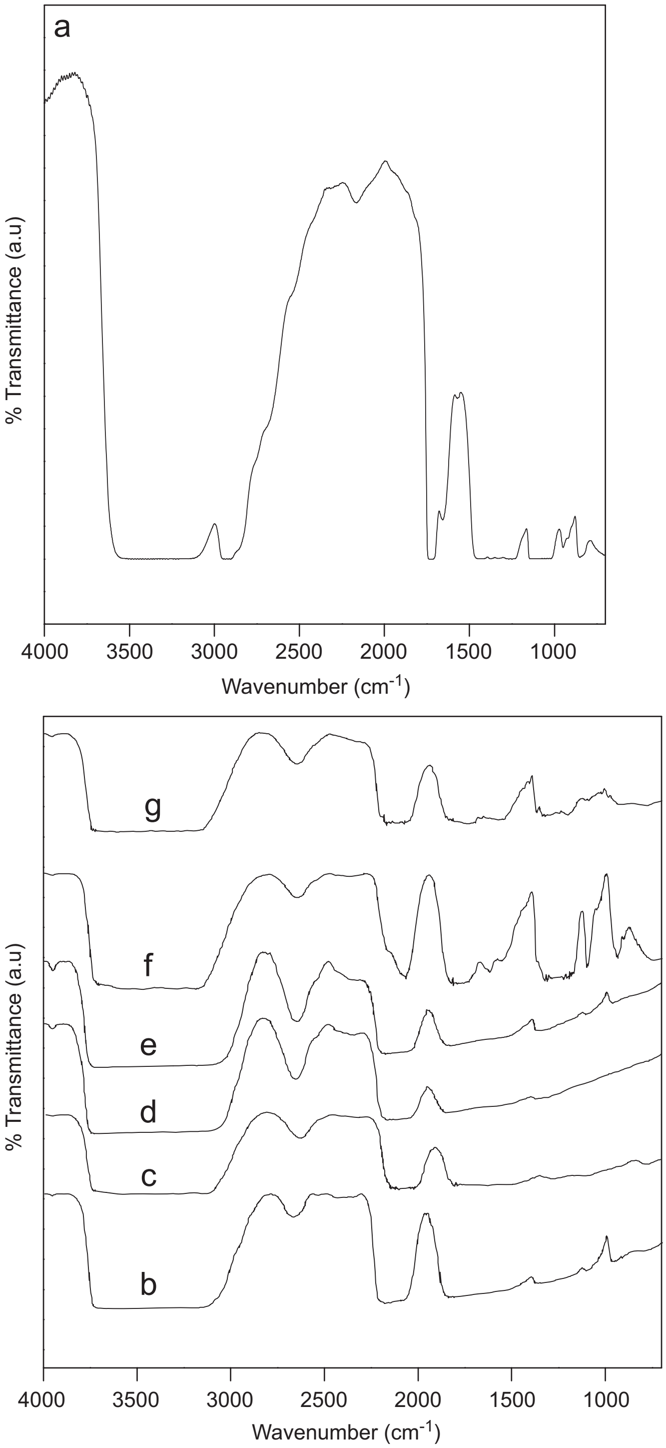

Fig. 2. FTIR spectrum of (a) pure PVA; and PVA doped with (b) 5 mol%; (c) 10 mol%; (d) 15 mol%; (e) 20 mol%; (f) 25 mol%; (g) 30 mol% NH_4Br.