Available online at www.sciencedirect.com
SCIENCE DIRECT®

Materials Letters 60 (2006) 1724 – 1727

materials letters

www.elsevier.com/locate/matlet

Studies on transparent and solid proton conductors based on $NH_4H_2PO_4$ doped poly(vinyl alcohol)

Hongting Pu *, Ping Huang

Institute of Functional Polymer, School of Materials Science and Engineering, Tongji University, Shanghai, 200092, China

Received 17 October 2005; accepted 3 December 2005
Available online 22 December 2005

Abstract

A novel transparent and anhydrous proton conductor, which can be used in solid electrochromic device (ECD), was prepared by mixing poly (vinyl alcohol) (PVA) with ammonium dihydrogen phosphate ($NH_4H_2PO_4$). X-ray diffraction, differential scanning calorimeter (DSC), and Infrared spectra were used to characterize the structure of PVA/$x$$NH_4H_2PO_4$ composite membrane. Proton conductivity of the composite membranes was studied by the complex impedance method. The proton conductivity of the composite membranes increases with increasing temperature and increases with increasing phosphate doping-level at first and then decreases with increasing phosphate content after a certain value of x. The highest proton conductivity is near the area of $x = 0.067$. The transmittance of the complex membranes always decreases with increasing doping level of phosphate.

Keywords: Proton conductivity; Poly(vinyl alcohol); Ammonium salts; Phosphate; Transmittance

1. Introduction

Smart windows are characterized by their ability to vary the throughput of radiant energy–visible light as well as solar radiation. This function can be obtained by incorporating an electrochromic material in the window. The effect of electrochromism has been known for many years, and it is based on the fact that certain materials change color by means of redox reactions [1–3]. A typical electrochromic device (ECD) is composed of five superimposed layers on one substrate or positioned between two substrates in a laminate configuration [3,4]. Normally the substrates are made of glass or flexible polyester foil. The central part of the five-layer construction is a pure ion conductor (electrolyte), which can be either liquid or solid electrolyte. This ion conductor bounds on an electrochromic layer (WO_3 being a typical example). On the other side of the ion conductor is a film serving as the ion storage, ideally with electrochromic properties complementary to those of the first electrochromic layer. This central three layer structure is positioned between electrically conducting transparent layers; the best material in terms of optical and electrical properties is In_2O_3:Sn (known as indium tin oxide, ITO), while SnO_2:F is less costly and readily available on large area glass panes [5,6].

In recent years much work and intense research activity have been devoted to the study and development of solid-state ECD [3,7,8]. Polymer composite electrolytes are under extensive investigation for applications in electrochromic devices and for other uses in solid-state electrochemical devices. The obvious requirements on the electrolytes for solid-state electrochromic devices are chemical compatibility with specific electrode materials, transparency, and anhydrous state. Many proton conducting membranes based on polymers complexed with inorganic acids (such as H_2SO_4 and H_3PO_4) have excellent proton conductivity [9–13]. However, the most widely studied proton conductors based on polybenzimidazoles and polyimides are opaque [12,13], while poly(vinyl alcohol) (PVA) blended with inorganic acids (such as H_2SO_4 or H_3PO_4) has excellent proton conductivity and optical properties [10]. Nevertheless, the high chemical activity of H_2SO_4 and H_3PO_4 is a drawback for its practical applications in ECD. In present work, an anhydrous proton conductor based on poly(vinyl alcohol) (PVA)/$NH_4H_2PO_4$ composite, which contains a less

---

* Corresponding author. Tel./fax: +86 21 65982461.
E-mail address: puhongting@mail.tongji.edu.cn (H. Pu).

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.12.005

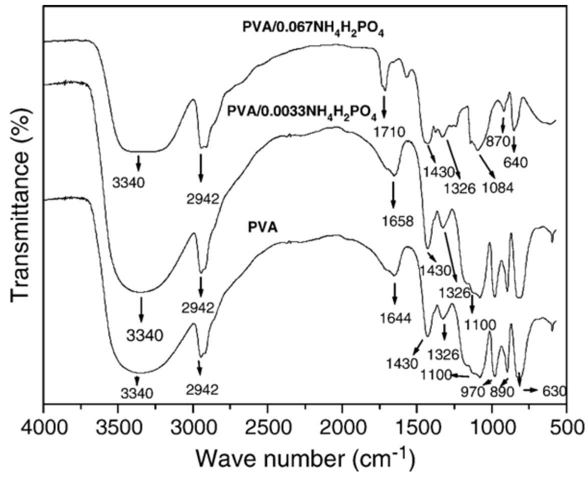

Fig. 1. FTIR spectra of PVA and PVA/xNH$_4$H$_2$PO$_4$ (x=0.0033 and 0.067) membranes.

stronger acidic moiety, is proposed. The proton conductivity, thermal stability, and transmittance of the composite membranes will be studied.

2. Experimental

The sample of PVA complexed with ammonium dihydrogen phosphate ($NH_4H_2PO_4$) under study was prepared by the solution-cast technique. The desired amount of PVA (Mn 17,200, Aldrich Co.) was dissolved in the boiling water and then cooled to 70 °C. The PVA aqueous solution was mixed with suitable amount of ammonium dihydrogen phosphate ($NH_4H_2PO_4$) (Shanghai Chemical Reagent Company, analytic grade and used as received) and stirred thoroughly for 5 h at 70 °C until forming aqueous solution, and then cast onto a polytetrafluoroethylene (PTFE) mold. After evaporated slowly at room temperature for one day, the membranes were dried completely in a vacuum oven to remove the water moieties. The PVA/x$NH_4H_2PO_4$ composite membrane was thus obtained, where x is molar ratio of NH_4^+ to repeat unit of PVA.

Infrared spectra were measured in transmission mode with a Nicolet Magna-550 spectrometer. The X-ray diffraction (XRD) patterns of the samples were measured at room temperature by a Rigaku D/Max 2550 Pe diffraction device, rotating anode X-ray generator working at 40 kV and 300 mA, with Cu Kα monochromatic radiation. The glass transition temperature of the composite membrane was measured by differential scanning calorimetry (DSC) (STA 449C, Netzsch), with a heating rate of 5 °C/min. Transmittance (800~200 nm) of the membranes with a thickness of 150 μm was measured by a double beam UV–VIS spectrophotometer with 760CTR (Shanghai Analysis Instruments Co., Inc.). The membrane for the proton conductivity measurement has a disk shape with a diameter of 1 cm and a thickness of 150 μm. The sample was sandwiched between stainless steel electrodes and was measured by Electrochemical Impedance Lab CHI 604B (CH Instruments, Inc.). The amplitude voltage was 0.005 V. The DC conductivity was calculated from a complex impedance plot (Cole–Cole plot) and was identical with the low frequency plateau of the AC conductivity.

3. Results and discussion

3.1. FTIR spectra of PVA/x$NH_4H_2PO_4$ membranes

FTIR spectra of PVA and its complexes with $NH_4H_2PO_4$ in different molar ratios were shown in Fig. 1. Comparing the spectra of different samples, it is observed that the complexed PVA materials exhibit almost similar (but not identical) characteristics to that of uncomplexed PVA. The band at 2942 cm^{-1} of asymmetric –CH$_2$-stretching and aliphatic C–H stretching of PVA, of which the content is constant in PVA, can be set as interior label. The relative intensity of other characteristic bands of PVA decreases a little with increasing NH_4^+ content. For instance, the band at 3340 cm^{-1} is the characteristic band of alcohols and phenols (–OH–) band, while the peaks at 1430 and 1326 cm^{-1} are the bending vibrations of –CH–OH. It is also found that the addition of the phosphate causes the shift of O–H bending vibration from 630 to 640 cm^{-1}, –CH$_2$-bending vibration from 1644 to 1710 cm^{-1} in the complexes (x=0.067). The peak that appeared at 970 cm^{-1} is absent in the complexes (x=0.067), which are suggested that intermolecular hydrogen bonds are formed between $NH_4H_2PO_4$ and PVA. The peak at 1100 cm^{-1}, assigned to C–O stretching of the secondary alcohol of PVA, is shifted to 1084 cm^{-1} in the complexes (x=0.067), and the intensity of this band in the complexes (x=0.0033) decreases. This may be attributed to the decreasing number of C–O groups in the complexes and the specific interactions in the polymer matrices. The FTIR spectra for the composite membranes prove the existence of complexation between the $NH_4H_2PO_4$ and PVA matrix.

3.2. XRD results and DSC thermogram of PVA/x$NH_4H_2PO_4$ membranes

Fig. 2 shows the X-ray diffraction patterns of PVA/xNH$_4$H$_2$PO$_4$ complex (x=0.067 and 0.0033) and PVA. It is shown that PVA has a semi-crystalline structure with the peak at 2v=20°. The intensity of PVA peak is reduced significantly after the addition of ammonium dihydrogen phosphate ($NH_4H_2PO_4$). On one hand, lower PVA content in the composite membrane results in the lower intensity of PVA crystalline peak at 2v=20°. On the other hand, the addition of

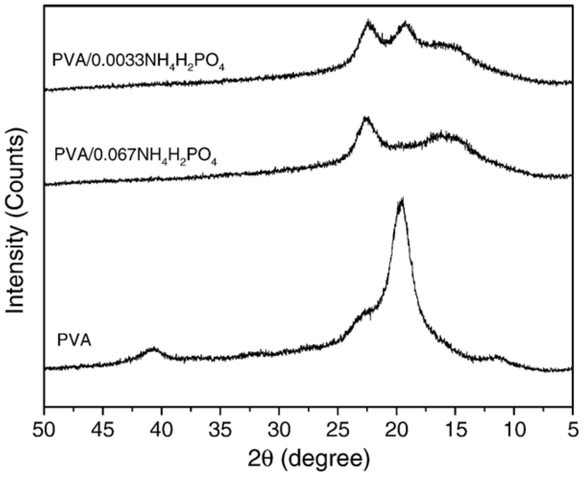

Fig. 2. X-ray diffraction of PVA and PVA/xNH$_4$H$_2$PO$_4$ (x=0.0033 and 0.067) membranes at room temperature.