Application of Proton Conducting Polymer Electrolytes to Electrochromic Devices

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Electrochromic display devices have been fabricated using Polydiallyldimethylammonium dihydrogenphosphate ($PAMA^+ H_2PO_4^-$) blended with H_3PO_4 as the electrolyte and WO_3 as the electrochromic film. The WO_3 deposited glass electrodes were doped with protons to form H_xWO_3 in which color depends on the charge density (CD) ranging from 0.01 to 0.04 C/cm^2. Proton conducting films of $PAMA^+ H_2PO_4^-$ 2 H_3PO_4 (2 moles of acid per polymer repeat unit) were sandwiched between two electrodes to obtain the following symmetric configuration: $Glass/ITO/WO_3/H^+$-electrolyte film/$H_xWO_3/ITO/Glass$. Prior to construction of the electrochromic windows, the electrochemical stability of polymer/acid blends was determined via cyclic voltammetry (CV).

Key Words: Electrochromic Window, Poly(diallyldimethylammonium dihydrogenphosphate), Proton Conductor
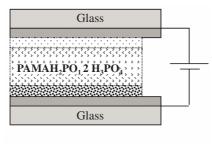
Introduction

An electrochromic device (ECD) is able to modify its optical absorption in a reversible and persistent way via the application of potential. The color changes either from transparent to colored or from one color to another depending on the electrochromic material and construction of the device. This phenomenon, which can be produced by the application of an electric field, is called electrochromism[1].

ECDs have numerous potential applications in technology. Thus, the possibility to modulate the diffuse reflectance lends itself to non-emissive display devices of different sizes. Modulation of the specular reflectance opens up possibilities for anti-dazzling rear view mirrors for automobiles and innovative architecture. Passenger cars with EC-based compartment rear-view mirrors have been available on the market for a few years. Modulation of the luminous transmittance can be used in future buildings for superior daylighting, and hence good working conditions, with a minimum electric of lighting. Other application may be for sun- glasses and also for windows in cars, trains, ships, etc.[2].

Many such devices can be viewed as variations on a basic design of five layers backed by a glass substrate according to the following (Figure 1):

i. A transparent electrically conducting film on the glass substrate;

ii. A thin film of electrochromic material;

iii. An electrolyte in liquid or solid form;

vi. A counter electrode operating in conjunction with the electrochromic material; and

v. An electrically conducting, transparent electrode,

Figure 1. Basic design of an ECD, indicating the transport of protons under the action of an electric field

The EC material and the counter electrode are mixed conductors for electrons and ions. Materials showing electrochromic properties include organic compounds (for example polyaniline) or inorganic materials such as Prussian blue and oxides such as WO_3, TiO_2, and NiO_x. The electrochromic redox reactions result in the coloring and bleaching of WO_3 (Eq. 1);

$$WO_3 + xH^+ + xe^- \xrightleftharpoons[\text{bleaching}]{\text{coloring}} H_xWO_3 \ (0 < x < 1) \tag{1}$$

By the application of an electric field between the external conducting electrodes (ITO), ions can be inserted into or extracted from the electrochromic film, whose optical properties thereby are altered. Depending on the electrolyte the ions can be H^+, Li^+, Na^+, K^+, H_3O^+, OH^- or their complexes[3−5]. The solid electrolyte can be either inorganic, such as hydrated oxide film, or organic (polymer). The requirements of the electrolyte are as follows:

a) An ionic conductivity greater than 10^{-5} S/cm, electronic conductivity less than 10^{-12} S/cm;

b) Electrochemical stability for extended cycling at operating temperature and during UV irradiation; and

c) Good adherence to the adjoining materials.

Several proton and ion conducting (such as Na^+, K^+) polymers for application in these devices have been published[5,6].

In this work, the electrochemical stability of $PAMA^+ H_2PO_4^-$ blends was determined by cyclic voltammetry (CV) studies. Electrochromic display devices were constructed using polydiallyldimethylammonium dihydrogenphosphate ($PAMA^+ H_2PO_4^-$) blended with H_3PO_4.

Experimental

$PAMA^+$ $H_2PO_4^-$ was obtained from poly(diallyldimethylammonium chloride) $PAMA^+Cl^-$ (Aldrich MW 200,000-350,000 g/mol) by the exchange reaction of the chloride with the dihydrogen-phosphate using an exchange resin. Proton conducting blends of composition $PAMA^+$ $H_2PO_4^-$ y H_3PO_4), where y denotes the number of moles of acid per polymer repeat unit, were prepared by mixing appropriate amounts of $PAMA^+$ $H_2PO_4^-$ with anhydrous phosphoric acid. Blends with $0.5 \leqslant y \leqslant 2.0$ could be cast into homogeneous transparent films. The synthesis and characterization data of the materials were published in our previous work[7].

Cyclic voltammograms were obtained with a potentiostat, type Princeton Applied Research Model M 173. Voltammograms of $PAMA^+H_2PO_4^-$ and $PAMA^+H_2PO_4^-$ 1 H_3PO_4 were recorded in a three electrode CV system, using a polymer modified Pt working electrode and a Pt counter electrode. The reference electrode was silver/silver chloride (Ag/AgCl) calibrated by a ferrocene/ferricinium redox system. Cyclic voltammetry studies were carried out in 0.1 M tetraethylammonium perchlorate-acetonitrile.

The WO_3 deposited ITO-coated glasses were obtained from Daimler-Benz Aerospace / Dornier GmbH - Germany. Before fabricating the devices, one of the WO_3 deposited electrodes was doped with protons in a solution of H_2SO_4 with pH $\sim$ 2.5 to form H_xWO_3. Several electrodes were doped with different charge densities (CD $\leqslant$ 0.04 C/cm^2). Proton conducting polymer electrolyte with y = 2 ($\sigma = 10^{-4}$ S/cm at RT) was sandwiched between H_xWO_3 and WO_3 coated glasses by increasing the temperature above 50 ^oC (T_g = -20°C for $PAMA^+H_2PO_4^-$ 2 H_3PO_4). Electrochromic windows with symmetric configuration Glass/ITO/WO_3/H^+-electrolyte film/H_xWO_3/ITO/Glass were obtained. UV/VIS-Spectra of electrochromic windows were recorded by Spectrometer Perkin Elmer Lambda 2.

Results and Discussion

Cyclic voltammograms of bare electrodes were obtained in an electrolyte of 0.1M tetraethylammonium perchlorate ($TEAClO_4$)/CH_3CN with different scan rates and the solution was electroinert from –1.750 to +1.750V.

Films were cast from the solution $PAMA^+$ $H_2PO_4^-$/acid in water. Then, ferrocene in the mg range ($\sim$ 1 mg) was dispersed into the film. The coated platinum electrodes were dried at 50°C overnight to remove any trace of free water. The voltammograms of $PAMA^+$ $H_2PO_4^-$ x H_3PO_4 (for x = 0 and x = 1) were recorded. Figure 2 represents the voltammograms in the presence of $PAMA^+$ $H_2PO_4^-$/ferrocene within the potential range of -1.5V/+1.5V with different sweep rates. The CVs of ferrocene in $PAMA^+$ $H_2PO_4^-$ versus Ag/Ag^+ (RE) showed symmetrical waves attributed to the reversible redox reaction between ferrocene/ferricinium ion with E_a = 0.410 V and E_c = 0.330 V. The shoulder near 0.600 V is attributed to the diffusion of the ferrocene to the Pt electrode at the anodic side and rediffusion at the cathodic side.

Figure 3 shows the studies of polyelectrolyte/ferrocene system between the -2 V to 2 V range. The strong peak at around +1.7 V is supposed to arise from the decomposition of the acid to yield P-O-P in the anodic scan followed with the decomposition of residual water in the cathodic cycle[8].
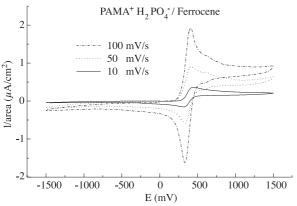
Figure 2. Cyclic voltammograms of PAMA$^+$ H$_2$PO$_4^-$/ferrocene system. Curves with scanx rate 100 mV/s is the 2nd sweep, 50 mV/s is the 3rd and 10 mV/s is the 4th.
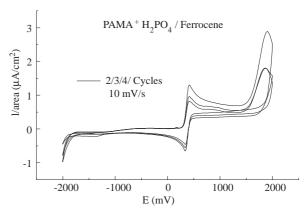
Figure 3. Cyclic voltammograms of PAMA$^+$ H$_2$PO$_4^-$/ferrocene system within –2.0 to 2.0 V potential range.

In both cases (Figures 2 and 3) the species leaving or entering the coating are detected with the anodic/cathodic currents. It is clearly observed that the thin film at the electrodes diminishes the intensities of the anodic and cathodic peak currents in subsequent cycling. Thus, the redox ions are ejected from the electrolyte to the solution. It can be concluded that the stability window for PAMA$^+$ H$_2$PO$_4^-$ extends over 3.25 V (from –1.9 to +1.7).

The voltammograms of PAMA$^+$ H$_2$PO$_4^-$ 1 H$_3$PO$_4$ were obtained in a three electrode system as explained before (Figure 4). Films were cast from the aqueous solution onto the Pt electrode without dispersing the ferrocene. The polymer film on the Pt electrode was dried overnight and inserted in a solution of TEAClO$_4$/CH$_3$CN.

It is clearly observed that the CV of x = 1 comprises no peak within the anodic sweep (0.1-1.5 V potential range). In the cathodic cycle, the formation of gaseous hydrogen was developed localized near the electrode and was subsequently reoxidized toward the anodic cycle. The material was stable within the 3 V range, i.e., -1.5 V to +1.5V.

Proton conducting films of x = 2 was sandwiched between two electrodes to obtain the symmetric configuration: Glass/ITO/WO$_3$/H$^+$-electrolyte film/H$_x$WO$_3$/ITO/Glass (Figure 1). The schematic representation of a solid state electrochromic display In$_2$O$_3$/H$_x$WO$_3$/ phosphotungustic acid/WO$_3$/In$_2$O$_3$ was already given[9].

During the coloration cycle, a negative voltage is applied to the WO$_3$ side, whereas bleaching of this electrode is achieved by reversing the polarity of the field. The application of a 1.5 V bias switches the color from the working electrode to the counter electrode and vice versa. The cell, which is represented in Figure 1, is reversible for prolonged cycling; however, the presence of moisture in the film distracts the WO$_3$ layer and makes the device irreversible.

Electrochromic cells consisting of H$_x$WO$_3$ layers with different proton charge density were prepared. By application of a 1.5 V bias with appropriate polarity, the blue color can be switched between the counter and working electrodes. Figure 5 shows the change of transmittance in the visible/near infrared spectral range. The performance of ECDs are controlled by the charge density (CD) injected into the WO$_3$. Thus, percent transmittance is decreased from ~50% to ~30% by varying the charge density. However, when CD > 0.04 C/cm^2, the electrodes become partially irreversible.
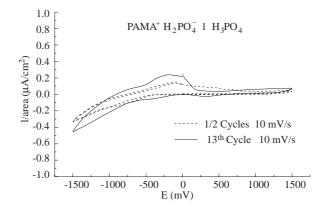
Figure 4. Cyclic voltammograms of PAMA$^+$ H$_2$PO$_4^-$ 1 H$_3$PO$_4$ in 0.1M TEAClO$_4$/acetonitrile

Within several days under open-circuit condition (OC) the H$_x$WO$_3$ electrode loses contrast. The loss of contrast is associated with the loss of H$^+$ due to rediffusion or oxidation. Figure 6 shows the change of transmittance due to such behavior for the cell with CD < 0.01 C/cm^2
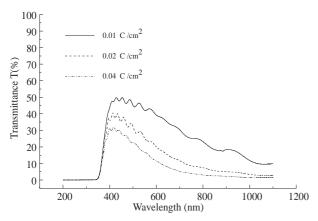

Figure 5. Spectral transmittance in colored states for ECDs where optical properties are varied with H$^+$-charge density
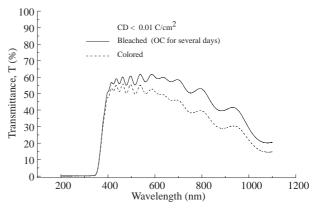

Figure 6. The effect of change of contrast on the transmittance of the EDC device

Conclusions

Cyclic voltammograms of the PAMA$^+$H$_2$PO$_4^-$ x H$_3$PO$_4$ are recorded on polymer modified working electrodes. It can be concluded that the stability domain for this material extends over 3.0 V.

Electrochromic devices based on PAMA$^+$H$_2$PO$_4^-$ 2 H$_3$PO$_4$ were constructed with a configuration glass/ITO/WO$_3$/ H$^+$-electrolyte film /H$_x$WO$_3$/ITO/glass. The application of a 1.5 V bias switches the color from the working electrode to counter electrode and vice versa. The constructed device is reversible for prolonged cycling in the absence of moisture.

Acknowledgments

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