

# Effect of pH value of poly(ethylenimine)–H<sub>2</sub>SO<sub>4</sub> electrolyte on electrochromic response of polyaniline thin films

Hailin Hu<sup>\*</sup>, Blanca E. Ortíz-Aguilar, Liliana Hechavarría

*Centro de Investigación en Energía, Universidad Nacional Autónoma de, UNAM, Priv.Xochicalco S/N, Temixco, Morelos 62580, Mexico*

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## Abstract

Electrochromic devices (ECDs) are electrochemical cells with one or two electrochemically active coatings that change color during the reduction–oxidation process. In this work an electrochromic polyaniline (PANI) thin film and a viscous electrolyte, formed by mixing a basic aqueous solution of polyethylenimine (PEI) and concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), have been used as the main components of an ECD. The pH value of the electrolyte is a function of the relative proportion between PEI and H<sub>2</sub>SO<sub>4</sub>. Fourier transform infrared spectroscopy (FT-IR) results show that for those PEI–H<sub>2</sub>SO<sub>4</sub> complexes of pH value varied from 2 to 9 sulfate ions of the inorganic acid are associated to the imine groups of PEI. If the pH value of the same system is lower than or equal to 1, HSO<sub>4</sub><sup>−</sup> anions appear in the electrolyte together with a notable reduction of the free water content. Electrochemical impedance spectroscopy study of these electrolytes show that the protonic conductivity of the PEI–H<sub>2</sub>SO<sub>4</sub> complex with pH 1 is almost three orders of magnitude lower than that of the same electrolytes but with a pH value between 2 and 6. Optical switch speed of a PANI/PEI–H<sub>2</sub>SO<sub>4</sub> based ECD at 550 nm under a square potential application of +1.2 V and −1.2 V is proportional to the ionic conductivity of the electrolyte of the device.  
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## 1. Introduction

Intrinsically conducting polymers are conjugated macromolecules that usually are electroactive under relatively low potential polarization. Some of these exhibit color change as they are oxidized or reduced in an electrochemical system and are called as electrochromic materials. Polyaniline (PANI) is one of the most studied conducting polymers with interesting electrochromic properties for smart window applications [1]. The reduced form of PANI (leucoemeraldine, LE) is transparent-yellow; the protonated semi-oxidized one (emeraldine salt, ES) is green; the deprotonated semi-oxidized form (emeraldine base, EB) is blue, and the fully oxidized state of PANI is dark blue-pur-

ple. A PANI based ECD can change the color from reduced state (transparent yellow) to oxidized state (green-blue) by applying a small negative or positive potential. In a previous work [2], it is reported that the presence of protons in PANI based ECDs is indispensable to keep the polymer electrochromically active during the redox state transitions. The protons can be originally presented in PANI(ES) or in the electrolyte, depending on the device sample preparation conditions.

To construct a solid electrochromic device (ECD), it is necessary the use of a solid or viscous electrolyte instead of a liquid one. Both polymethyl methacrylate (PMMA) with dissolved LiClO<sub>4</sub> and poly(ethylenimine) (PEI) mixed with a concentrated H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> have been used as viscous electrolytes for PANI based ECDs [3,4]. In the latter case, aqueous solution of PEI shows a basic characteristic due to the imine groups (NH<sub>2</sub>) on the lateral chains of

<sup>\*</sup> Corresponding author. Tel.: +52 55 56229747; fax: +52 55 56229742.  
E-mail address: [hzh@cie.unam.mx](mailto:hzh@cie.unam.mx) (H. Hu).

the macromolecule. By mixing with a concentrated acid, an exothermal reaction occurs and a complex system of PEI–inorganic acid is formed. As the presence of protons is necessary for electrochromic properties of PANI, it is supposed that the concentration of protons in the PEI–H<sub>2</sub>SO<sub>4</sub> electrolyte would affect directly the performance of a PANI based ECD. Based on this hypothesis, it is tried to study in this work the effect of pH value of the polyelectrolyte PEI–H<sub>2</sub>SO<sub>4</sub> on the optical response of PANI based ECDs. Both simple and composite PANI thin films with poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) have been prepared for comparison purpose.

## 2. Experimental

Thin films of PANI and PANI–PAMPS were prepared with a solution bath method as reported previously [2]. Indium–tin oxide coated conducting glass sheets (ITO,  $R \approx 8\text{--}12 \Omega/\square$ , Delta Technologies, Ltd., USA) were used as substrates for polymeric film deposition. The chemical bath consisted in 30 ml of 2 M HCl aqueous solution, 1 ml of PAMPS (Aldrich, 15 wt% in water with an average molecular weight of 250,000) in the case of the PANI–PAMPS composite films, 0.4 ml of distilled aniline, and 60 ml of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 0.1 M aqueous solution. The clean ITO glass substrates were introduced into the bath under magnetic stirring and kept at a temperature of 3–5 °C. After 1 h of deposition thin films of PANI or PANI–PAMPS of about 100 nm of thickness were formed on ITO substrates.

The polyelectrolyte PEI–H<sub>2</sub>SO<sub>4</sub> was prepared by mixing the water solution of a branched PEI,  $-(\text{NHCH}_2\text{CH}_2)_x$   $[-\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)\text{CH}_2\text{CH}_2-]_y$  (Aldrich, 50 wt% in water with an average molecular weight of 750,000, pH ~ 10), and concentrated sulfuric acid (JT Baker, 98.4%). Because the exact monomer structure of PEI is unknown, the volume proportion between PEI and H<sub>2</sub>SO<sub>4</sub> was used in this work as an indicator of the composition of the PEI–H<sub>2</sub>SO<sub>4</sub> complexes. An ECD was constructed by applying one of these PEI–H<sub>2</sub>SO<sub>4</sub> electrolytes on free surface of a PANI or PANI–PAMPS film and then collocating another ITO surface (auxiliary-electrode of the device) onto the viscous electrolyte to form a sandwich structure of glass/ITO/PANI or PANI–PAMPS/PEI–H<sub>2</sub>SO<sub>4</sub>/ITO/glass. Finally the sandwich was sealed with epoxy to avoid solvent evaporation of the electrolyte. The thickness of the PEI–H<sub>2</sub>SO<sub>4</sub> electrolyte was about 50 μm. The electrical contacts of the ECDs were the two ITO coatings and the effective area of the devices was about 1.2 cm<sup>2</sup>.

Optical transmittance spectra as well as optical kinetic responses of the PANI based ECDs were recorded on a Shimadzu spectrophotometer UV–VIS–NIR model UV3101PC. A homemade voltage control unit was used as the electrical voltage pulse source for these ECDs. FT-IR spectra of the PEI solution and its complex with H<sub>2</sub>SO<sub>4</sub> were obtained on ATR mode on a Perkin–Elmer FT-IR spectrophotometer System 2000-Spectrum GX.

Ionic resistance of PEI–H<sub>2</sub>SO<sub>4</sub> polyelectrolytes was determined by electrochemical impedance spectroscopy (EIS) on a Solatron SI1260 Impedance/Gain-Phase Analyzer coupled with a SI 1287 Electrochemical Interface.

## 3. Results and discussion

Fig. 1 shows the pH value of PEI–H<sub>2</sub>SO<sub>4</sub> polyelectrolytes as a function of volume proportion between their two components as well as the free water content of these complexes. Assuming that the weight loss of an aqueous sample corresponds to its free water content, the last parameter was measured by heating our complex samples at 80 °C in air for 24 h. The interest for knowing the free water content in a protonic conductor is because protons contributing to conduction are those associated to freely rotating water molecules in the form of hydronium groups (H<sub>3</sub>O)<sup>+</sup>. Therefore free water content in PEI–H<sub>2</sub>SO<sub>4</sub> complexes should be an important parameter that is related to their protonic conductivity. In the case of PEI, which is a basic, aqueous and viscous solution, it was observed that its weight loss was about 40% after the heat treatment. Taking into account that the original PEI sample contains a 50 wt% of water, it suggests that the difference of 10 wt% is due to tightly bonded water molecules in the polymer.

The mixture of PEI and H<sub>2</sub>SO<sub>4</sub> is an acid–base reaction, and its product should show a different molecular structure than the original reagents. Fig. 2 exhibits FT-IR spectra of PEI (curve a) and PEI–H<sub>2</sub>SO<sub>4</sub> complexes (curves b–e) with different pH value. The assignments of the absorption bands of the spectra are listed in Table 1. At the moment

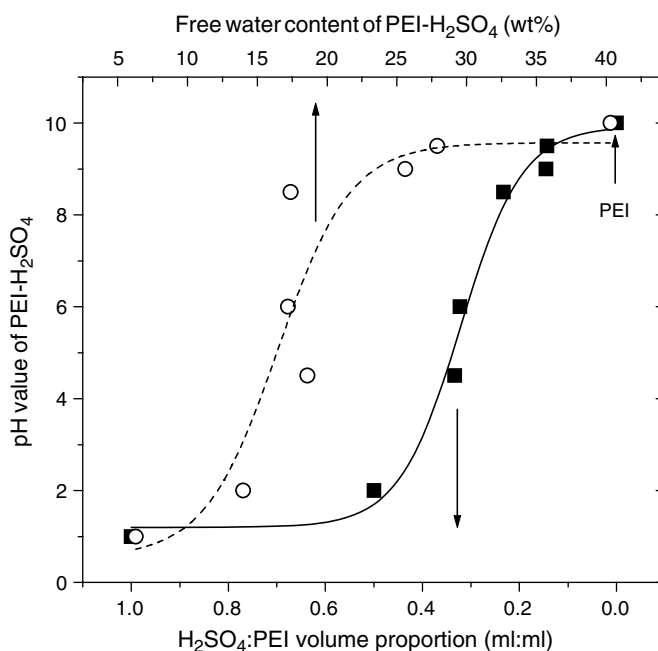


Fig. 1. pH value of PEI–H<sub>2</sub>SO<sub>4</sub> polyelectrolytes as a function of their free water percentage (open circles) as well as H<sub>2</sub>SO<sub>4</sub>:PEI volume proportion (solid squares). The continue traces are fitting curves of the experimental data.

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