

# Optical Properties of an Electrochromic Device Based on Poly (aniline 2-sulfonic) acid (PASA) Film, Formed by Ionically Self-Assembled Multilayers (ISAM) Technique

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## Abstract

A new ElectroChromic Device (ECD) was designed and constructed based on Ionically Self Assembled Multilayers (ISAM) technique, in which oppositely charged polymers are used to construct films of multiple layers. The ECD device proposed and studied in this work was based on Poly (aniline 2-sulfonic) acid, (PASA), as the active electrochromic polyanion, and Poly (allylamine hydrochloride), (PAH), as the inactive polycation. Cyclic Voltammetry (CV) technique was employed to study redox properties of the polymer film and to help to determine the operating voltage of the device. It was determined that the PAH/PASA ECD has two redox states between  $-700\text{mV}$  and  $+700\text{mV}$ . The ECD with 40 bilayers demonstrated dark green to light brown to dark gray electrochromism, in the  $-700\text{mV}$  to  $+700\text{mV}$  window. The major transmittance occurred at  $-600\text{mV}$  (dark green) and  $+600\text{mV}$  (dark gray). The ECD in the relaxed state, i.e. no voltage applied, is light brown. At  $-600\text{mV}$ , in visible spectrum, the highest contrast ( $\Delta T=27\%$ ) appeared at approximately  $690\text{nm}$  (dark green) and at  $+600\text{mV}$  the highest transmittance in visible range was a broad range between approximately  $600\text{nm}$  to  $710\text{nm}$ .

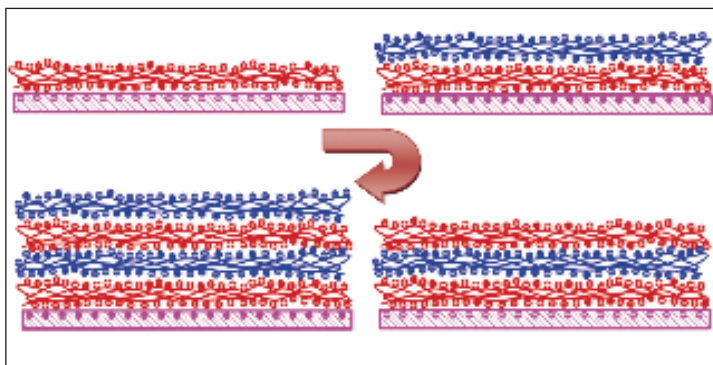
**Keywords:** Electrochromic, Ionically Self Assembled Monolayers, ISAM, Poly (aniline 2-sulfonic) acid, PASA

## 1. Introduction

ECDs are devices that are constructed of thin polymer film on conductive material. The polymer film reacts to voltage by changing color and/or optical density.

The color change is reversible by reversed voltage and it is because of the redox properties of the electrochromic polymer(s). When applying voltage, the electron flow will change the electronic structure of the electrochromic material by reducing or oxidizing it, this change in structure appears as a change in color and/or optical density. To date, some of the known applications of optical switching are seven-segment displays<sup>[1]</sup>, anti-glare mirrors<sup>[2]</sup> and solar-attenuated windows<sup>[3]</sup>. Other possible future application of ECDs is in flat panel displays.

In this work we report the electrochromic properties of Poly (aniline 2-sulfonic) acid, (PASA) which was used as a polyanion. Poly (allylamine hydrochloride), (PAH), a non electrochromic polyelectrolyte, was used as the polycation to help form the layers of polymer film. In forming the polymer film, we used one electrochromic polymer only; however two oppositely charged electrochromic polymers can also be used to form a polymer film. Such a device is called Complementary ElectroChromic Device, CECD.<sup>[4,5]</sup> CECDs are expected to have more redox states compared to ECDs with just one electrochromic polymer. ISAM technique was employed to construct the polymer film on the substrate. In this method opposite charged polymers are used to buildup several layers of polymers on the Indium Tin Oxide (ITO) coated glass substrate. Due to the opposite charge



**Figure 1.** ISAM technique, layers of opposite charged polymers are used to construct the thin polymer film.

of neighboring layers, layers bind together to form the polymer film as shown in Figure 1.

ISAM technique makes it possible to have nanometer control on the thickness of the film. The formed films are very homogenous and smooth. Strong ionic interactions between cationic and anionic layers make very stable and robust films.

## 2. Procedure

### 2.1 Substrate

A 25mm x 75mm x 0.7mm unpolished float glass,  $\text{SiO}_2$  passivated with ITO coating on one surface ( $R_s = 8 - 12 \Omega/\text{sq}$ ) was used as the conducting substrate (Delta Technologies, USA). The non ITO surface and about 20 mm of the ITO coated side of the slide was covered by electrical tape to prevent any ISAM film deposition. Then the slide was cleaned with Acetone and washed with Deionized (DI) water and dried with nitrogen before the deposition of the ISAM film.

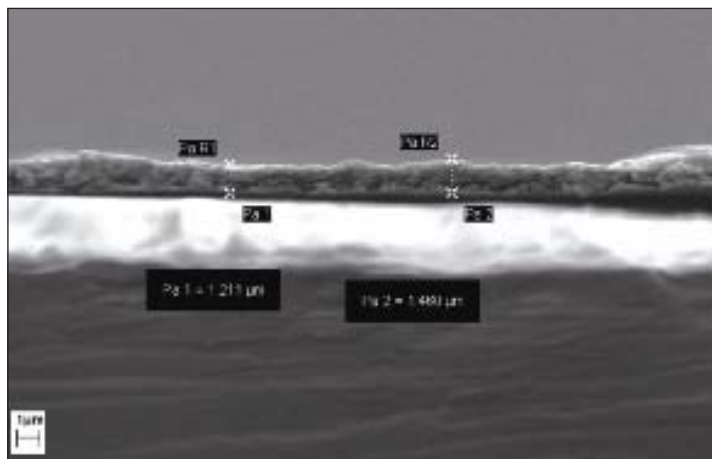
### 2.2 Solutions

All chemicals were reagent grade and were used as received. DI water was used throughout the entire solution preparation process. All chemicals were commercially available (Sigma-Aldrich, USA). 2mM PASA solution (pH 3) was used as polyanion and 10mM PAH (pH 9) was used as polycation. Both solutions are water based and freshly prepared prior to use.

### 2.3 Film Deposition

ISAM technique was used to deposit thin film of PAH (polycation) / PASA (polyanion) on the substrate. Substrate was washed with DI water prior to the deposition process to provide a negatively charged surface. Deposition was done at room temperature, using an automatic dipping machine.

To form the first bilayer the sample was: 1) exposed to PAH by spinning it in PAH bath for 4 minutes; 2) then washed in three steps, 45 seconds each, with DI water to wash off any



**Figure 2.** SEM image of 40 bilayers of PAH / PASA on ITO

loosely bound PAH molecules. After forming the first monolayer, the sample was; 3) exposed to PASA by spinning it in PASA solution for 5 minutes and then; 4) washed with DI water in three steps, 45 seconds each, to remove any loosely bound PASA molecules. These four steps were to form one bilayer, consist of one polycation and one polyanion layer. This process was repeated 40 times to form a thin PAH / PASA film of 40 bilayers. This process can be repeated any desired number of times and can be use to control the thickness of the ISAM film. The electrical tapes were then removed. Scanning Electron Microscopy (SEM) was used to investigate thickness of the ISAM film. The thickness of each bilayer is estimated to be 30 – 35 nm. The cross section of the film showed homogeneity as shown in Figure 2.

## 3. Results and Discussion

### 3.1 Cyclic Voltammetry

After constructing the PAH/PASA thin film, a three electrode CV technique was performed to characterize the electrochemical properties of PAH/PASA film in 0.1M  $\text{NaClO}_4$  aqueous electrolyte solution. A Standard Calomel Electrode (SCE) was used as the reference electrode and a platinum flag (wire) as the counter electrode. The polymer film was scanned at 200mV/s from  $-600 \text{ mV}$  to  $+1400 \text{ mV}$  to investigate the redox states. From the CV data operating voltage was determined to be in between  $-600 \text{ mV}$  and  $+600 \text{ mV}$ . The oxidation peak appears at approximately  $+600 \text{ mV}$  and reduction peak appears at approximately  $-600 \text{ mV}$  as shown in Figure 3.

### 3.2 Electrochromic Switching in Salt Solution

The electrochromic device was then immersed in 0.1 M  $\text{NaClO}_4$  aqueous solution and the voltage was applied across the device and a copper electrode that was also immersed in the solution. The voltage was varied from  $-700 \text{ mV}$  to  $+700 \text{ mV}$  and

two color changes were observed at  $-600\text{mV}$  and  $+600\text{mV}$ , as it was predicted from the CV data as shown in Figure 4.

### 3.3 Results

To further illustrate the redox properties of the electrochromic material, we studied the optical properties of PAH/PASA device using the UV-Vis. spectroscopy method. In this method a concentrated beam of electromagnetic waves with varying wavelength from  $400\text{nm}$  to  $1100\text{nm}$  was shined at the device and the transmitted wave was collected at the other end of the apparatus for detail analysis of transmittance and absorbance behaviors of the device.

#### 3.3.1 Absorbance

At  $-600\text{mV}$  the lowest absorbance in the visible range occurred at approximately  $510\text{nm}$ , which corresponds to the dark green color of the film, and the highest absorbance occurred at approximately  $690\text{nm}$  as shown in Figure 4 and 5.

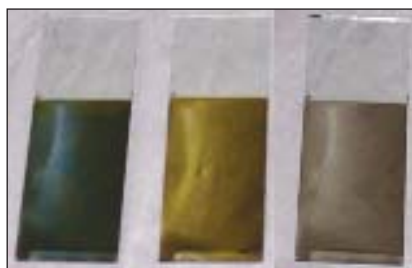


Figure 4. Color change of 40 bilayers of PASA at different voltages. From left to right, at  $-600\text{mV}$ ,  $0.0\text{mV}$ , and  $+600\text{mV}$ .

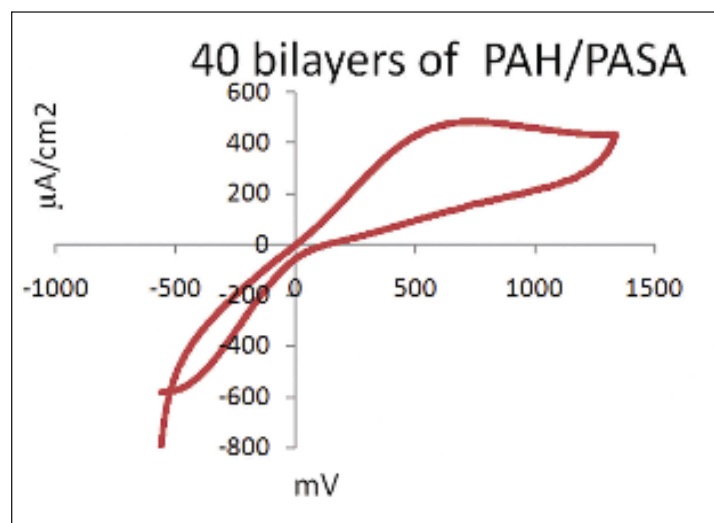


Figure 3. Cyclic Voltammetry of PAH/PASA at  $200\text{mV/s}$  scan rate, oxidation peak can be seen at  $\sim +600\text{mV}$  and reduction is predicted to be at  $\sim -600\text{mV}$ .

the gray color of the film as shown in Figure 4 and 5.

#### 3.3.2 Transmittance

The highest transmittance difference was observed between the  $-600\text{mV}$  reduction peak and the neutral line. This showed an approximately 27% ( $\Delta T=27\%$ ) contrast, which appeared at approximately  $690\text{nm}$  wavelength as shown in Figure 6.

The highest contrast for the  $+600\text{mV}$  oxidized state was approximately 25% ( $\Delta T=25\%$ ) which was observed at approximately  $480\text{nm}$  wavelength.

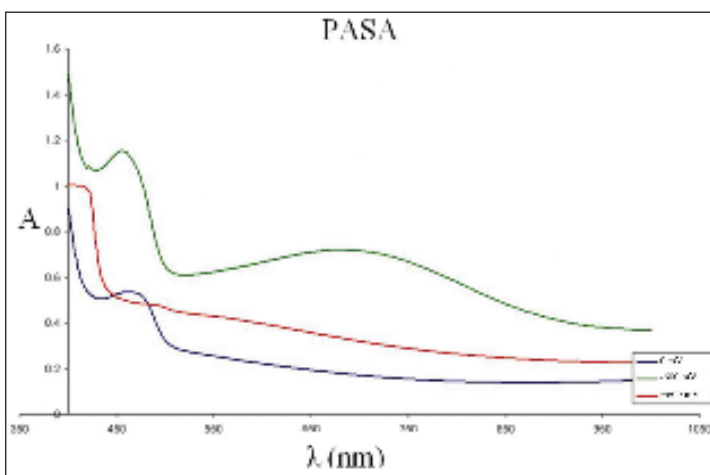


Figure 5. Absorbance measurements of PAH/PASA device at  $-600\text{mV}$  (reduction state) and  $+600\text{mV}$  (oxidation state) in comparison with the absorbance of the device at neutral state ( $0\text{mV}$ ).

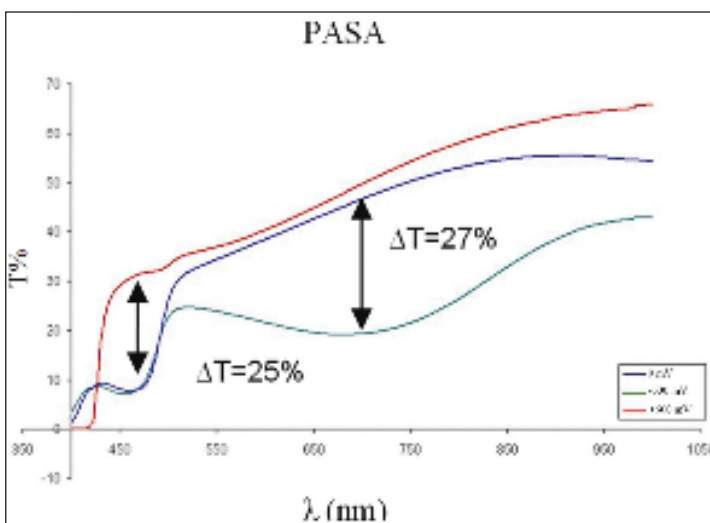


Figure 6. Transmittance measurements of PAH/PASA device at  $-600\text{mV}$  (reduction state) and  $+600\text{mV}$  (oxidation state) in comparison with the transmittance of the device at neutral state ( $0\text{mV}$ ). The highest contrast is about 27% that is observed at  $\sim 690\text{nm}$ , and is between reduced and neutral states.

## 4. Conclusions

Redox properties of a system based on PASA was demonstrated in this paper. PASA was found to have promising electrochemical and spectral properties. PASA has two redox states in the  $-1.0\text{V}$  to  $+1.0\text{V}$  range. The color change remains after disconnecting the voltage, which confirms that the electrochromic device based on PAH and PASA polymers has long term memory. According to the CV data, the polymer film oxidizes at  $+600\text{mV}$  and reduces at  $-600\text{mV}$ . The device changes color at both oxidation peak ( $+600\text{mV}$ ) and reduction peak ( $-600\text{mV}$ ) which agrees with the results from the CV. The device showed about 25% contrast at the oxidation peak and about 27% contrast at the reduction peak.

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Reza Montazami received his B.S. in Physics and Astronomy from Virginia Tech in 2007. He is currently pursuing a Ph.D in Materials Science and Engineering at Virginia Tech.