

Study of Poly(Methyl Methacrylate)-Based Gel Electrolyte for Electrochromic Device

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Electrochromic devices are reported by using polyaniline (PANI) doped with poly(styrene sulfonic acid) (PSS) as coloring electrodes, poly(ethylenedioxythiophene)-poly(styrene sulfonic acid) (PEDOT-PSS) as complementary electrodes, and poly(methyl methacrylate)(PMMA)-based electrolyte as gel electrolyte. Characterizations of the PANI-PSS are performed using Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and UV-vis spectroscopy (UV). The spectroelectrochemical and electrochromic properties of electrochromic devices are investigated, electrochromic device based on PMMA-based gel electrolyte shows larger coloration efficiency, larger optical contrast, and faster response time than that based on liquid electrolyte at long term cycles.

Keywords: Gel electrolyte, polyaniline, poly(styrene sulfonic acid), electrochromic device, spectroelectrochemistry, coloration efficiency

1. INTRODUCTION

Recent developments of new solid or gel state materials for electrodes have drawn keen interest from the researchers working in the area of electrical power generation and storage systems. Among them, the recent ones are the polymer electrolytes [1-10]. Polymer electrolytes are promising materials because of its wider applications in electrochromic devices (ECD), modified electrodes, sensors, supercapacitors, electric vehicles (EV), high vacuum electrochemistry, thermoelectric generators, and solar cells [11-12]. One of the great challenges is to develop ECD using electrolyte types. The

electrolytes must be ionically conductive, but electronically insulating. Liquid-state electrolytes usually has several inevitable drawbacks such as leakage of electrolyte solution, low chemical stability, and hydrostatic pressure considerations, and is unsuitable for scaling-up to large-area devices. Therefore, a liquid-state electrolyte is difficult to seal and not safe for practical application. Gel state electrolyte (GPE) is fabricated in an anhydrous environment by dissolving host polymer into a highly hydroscopic liquid electrolyte and casting the polymer solution at elevated temperatures (120–140 °C), followed by cooling the cast thin solution to form the gel electrolyte film. Accordingly, adoption of the gel electrolyte would reduce the possibility of leakage of the electrolyte.

Among the polymer matrixes that are promising for the application in GPE, polyacrylonitrile (PAN) [13,14], poly(methyl methacrylate) (PMMA) [15], and poly(ethylene oxide) (PEO) [16] based polymers have been most extensively studied. Poly(methyl methacrylate) (PMMA)-based electrolyte has a special significance because of its well-known chemistry and cheaper method of processing them as laminates.

Conducting polymers (CPs) are also actively pursued for the electrodes in the last few decades [17-36]. Several discoveries brought the CPs to full commercialization with applications in thin-film transistors [37], displays [38], sensors [39], polymer light-emitting diodes [40], photovoltaics [41], and electrochromic devices [42]. Among them, electrochromic materials show a reversible optical change ability in absorption or transmittance upon electrochemically oxidized or reduced, which has stimulated the interest of scientists [43]. The electroactive conducting materials such as polypyrroles, polyanilines, polycarbazoles, polytriphenylamines, polythiophenes, and poly(ethylenedioxythiophene)-poly(styrene sulfonic acid) (PEDOT-PSS), etc. have been widely studied to obtain target polymers with superior properties. Among them, polythiophenes are an important representative class of conducting polymers that can be used as electrical conductors. Accordingly, the electrochromic devices have been fabricated using complementary electrochromes on adjacent electrodes, such as polyethylenedioxythiophene (cathodically darkening) and polyaniline (anodically darkening), which have been shown to provide additive contrast [44].

In the present work, hybrid polymer electrolyte films that consist of PMMA, PC, and LiClO₄ are prepared. We also report the synthesis and properties of electrochromic PANI-PSS films. The electrochemical and physicochemical properties of the PANI-PSS films have been characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and UV–vis spectroscopy (UV). Its dual-type high-quality ECD was constructed with poly(ethylenedioxythiophene)-poly(styrene sulfonic acid) (PEDOT-PSS) electrode and PMMA-based polymer electrolytes. The specreoelectrochemistry and electrochromic switching of the electrochromic devices were studied.

2. EXPERIMENTAL

2.1. Preparation of PANI-PSS

Polyaniline was prepared by the oxidative polymerization of aniline (Merck) with ammonium peroxydisulfate (APS) in HCl (Merck) aqueous solution at 5 °C as described elsewhere [45]. Solution

of PANI-HCl in m-cresol was prepared. PANI-HCl electrode was obtained by spin coating (1000 rpm for 1 min) of PANI-HCl thin film over the surface of ITO. The PANI-HCl put in oven for 24 hours at 70 °C to remove m-cresol. Before each experiment, ITO was cleaned in an ultrasonic bath using detergent, deionized water, and isopropanol, and then dried with a dry nitrogen flow, followed by UV-O₃ treatment for 30 min. The Emeraldine base form (EB) of PANI was obtained by treating the PANI-HCl film in 0.1 M ammonium hydroxide (Aldrich) for 5 min. The EB film was then redoped with PSS (PANI-PSS). PEDOT-PSS (Alfa) electrode was prepared by spin coating (1000 rpm for 30 s) of PEDOT-PSS thin film on the surface of ITO, and then allowed to dry at 150 °C for 3 min. A thin film of PEDOT-PSS was formed over a cleaned indium tin oxide (ITO) electrode (1.0 × 1.0 cm²).

2.2. Preparation of the gel electrolyte and fabrication of electrochromic device

A 0.1 M LiClO₄ in propylene carbonate (PC) (Alfa Aesar) and PMMA (M_w = 150,000, ACROS) solution (Table 1) was prepared and the polymer electrolyte solution (the thickness of PMMA+PC+LiClO₄ layer is 458 μm and the ionic conductivity is about 1.4×10⁻³ S/cm) was injected between PANI-PSS and PEDOT-PSS electrodes to form a ITO|PANI-PSS||PMMA-PC-LiClO₄||PEDOT-PSS|ITO device (device b, Fig. 1). Edges of the device were sealed with epoxy resin to prevent the junction from the attack by moisture and oxygen. The resulting electrochromic device had an effective area of about 1 cm². For comparison, 0.1 M LiClO₄ in propylene carbonate (PC) as electrolyte solution was using a method similar to form a ITO|PANI-PSS||PC-LiClO₄||PEDOT-PSS|ITO device (device a).

Table 1. Polymer electrolytes with various PC concentrations.

	Conductivity (S/cm)	T (%)	State
1 M LiClO ₄ in PC	6.67 × 10 ⁻³	95.8	liquid
1 M LiClO ₄ in PMMA+PC	1.40 × 10 ⁻³	94.4	gel

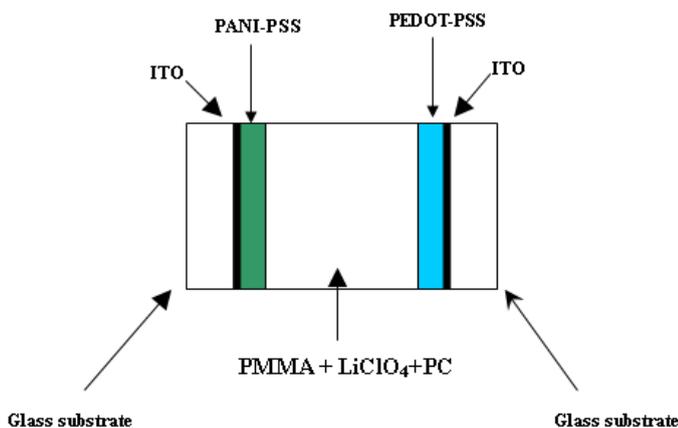


Figure 1. Schematic diagram of ITO|PANI-PSS||PMMA-PC-LiClO₄||PEDOT-PSS|ITO device.

2.3. Characterizations

The Fourier transform infrared (FT-IR) spectra of PANI-HCl (emeraldine salt), emeraldine base (EB), and PANI redoped with PSS (PANI-PSS, emeraldine salt) in KBr pellets were obtained using a Perkin Elmer FT-IR instrument with a resolution of 4 cm^{-1} . The average of 16 scans was used to obtain each spectrum. All samples were vacuum-dried overnight prior to measurement. An X-ray photoelectron spectroscopy (XPS) study was performed using an ESCA 210 spectrometer with Mg K α ($h\nu = 1253.6\text{ eV}$) irradiation as the photon source. The primary tension was 12 kV and the pressure during the scans was approximately 10^{-10} mbar.

2.4. Electrochemistry and spectroelectrochemistry

Electrochemical studies were performed with CHI627D electrochemical analyzer (U.S.A.). All experiments were carried out in a three-component cell. An Ag/AgNO₃ (3 M TBAP/acetonitrile) electrode, platinum wire, and ITO coated glass plate (1 cm^2 area) as reference, counter and working electrodes. A Luggin capillary, whose tip was set at a distance of 1-2 mm from the surface of the working electrode, was used to minimize errors due to iR drop in the electrolytes. Spectroelectrochemical studies were performed with Agilent Cary 60 UV-Visible spectrophotometer to record the in situ UV-Visible spectra by operating in time course mode. UV-Visible spectroelectrochemical experiments were done in a quartz cuvette of 1 cm path length assembled as an electrochemical cell with an optically transparent working electrode, a platinum wire as counter electrode and Ag/AgNO₃ as reference electrode.

3. RESULTS AND DISCUSSION

3.1. Characterizations of PANI-PSS

The FT-IR spectra of doped PANI (oxidative polymerization of aniline with ammonium peroxydisulfate in HCl medium), dedoped PANI (EB), and PANI-PSS (PANI redoped with PSS) are shown in Fig. 2a-c, respectively. The doped PANI (doped with HCl, curve a) exhibits some peaks. The absorption peak at 810 cm^{-1} is attributed to the para-substituted aromatic out-of-plane bending. The -C-N stretching vibration of PANI is observed clearly at 1300 cm^{-1} . The main characteristic peaks at 1560 and 1480 cm^{-1} are ascribed to the stretching vibrations of the -C=N quinonoid and the -C=C benzenoid rings of PANI doped with HCl, respectively [20]. Dipping the emeraldine salt of PANI with ammonium hydroxide yields the dedoped form of PANI, whose two main characteristic peaks (1560 and 1480 cm^{-1}) shift to 1590 and 1500 cm^{-1} (curve b), respectively. After the dedoped form of PANI is redoped by PSS doping time at 300 s (curve c, PANI-PSS, emeraldine salt), the two main characteristic peaks shift to about 1575 and 1485 cm^{-1} , respectively. This indicates that PANI can be doped with PSS via a simple doping-dedoping-redoping technique.

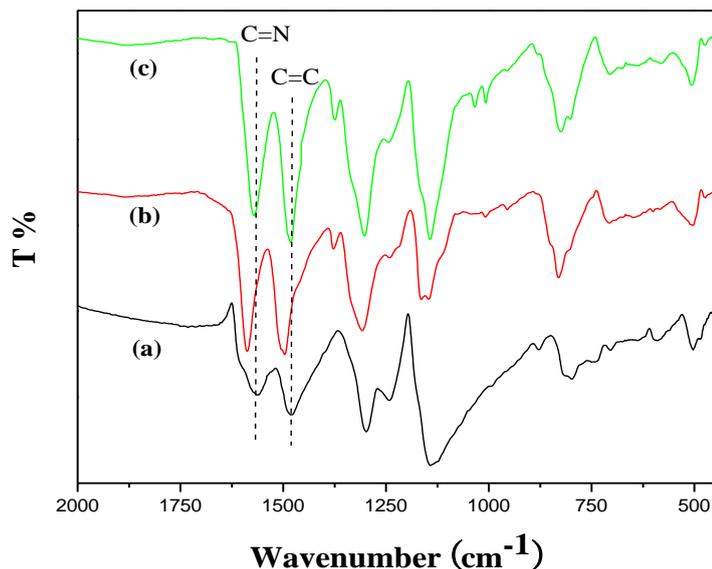
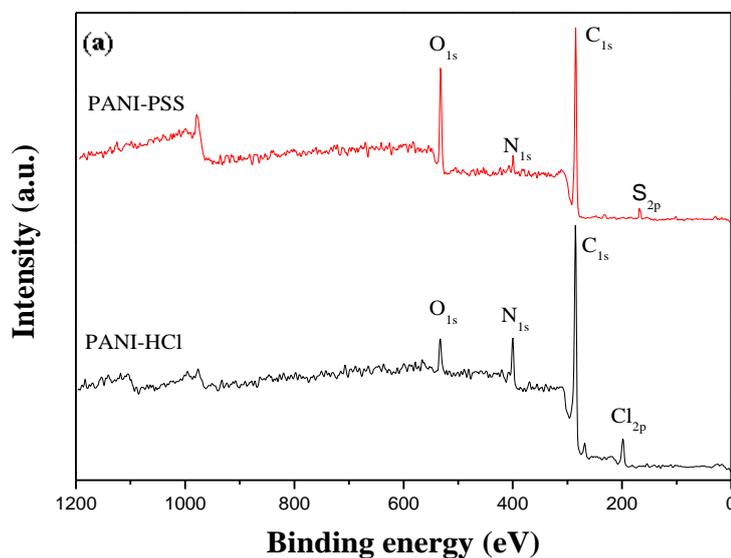


Figure 2. FT-IR spectra of (a) PANI-HCl (emeraldine salt), (b) emeraldine base (EB) PANI, and (c) PANI redoped with PSS (PANI-PSS, emeraldine salt).

Figure 3a shows the survey scan of the PANI-PSS and PANI-HCl composite materials. It is evident from the spectra that the survey scan of the PANI-PSS composite is similar to that of the spectra obtained for the PANI-HCl. The PANI-PSS with the signals due to C_{1s} , N_{1s} , O_{1s} , and S_{2p} can be also seen. The XPS spectrum of core-level N_{1s} for PANI-PSS is shown in Fig. 3b. The signals of N_{1s} were fitted with peaks at 398.7, 399.6, 400.5, and 401.4 eV, which corresponded to quinonoid imine ($=N^-$), benzenoid amine ($-NH-$), protonated amine ($-N^+$), and protonated imine ($=N^+$), respectively. Kumar et al. [46] attributed the last two peaks to the presence of polarons (radical cations) and bipolarons (dications), respectively. The ratio of these two N_{1s} components at 400.5 and 401.4 eV (positively charged nitrogen atoms) could be considered as a direct estimation of the doping level of PANI [47]. The $[-N^+ + =N^+]/N$ doping levels are 39 % for PANI-PSS.



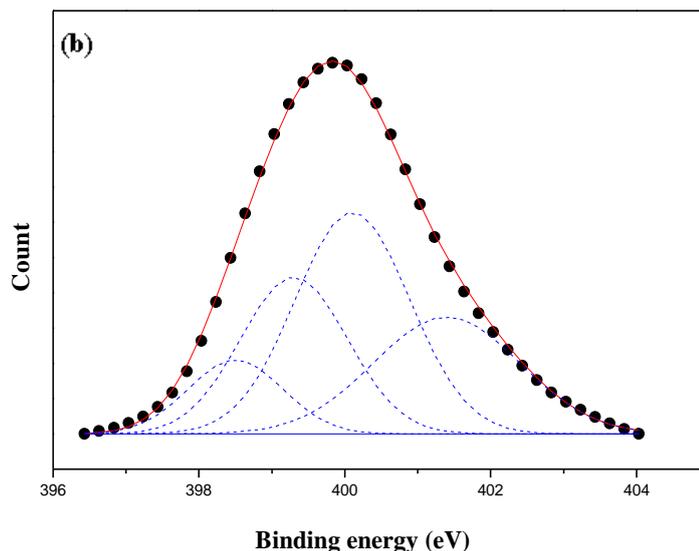
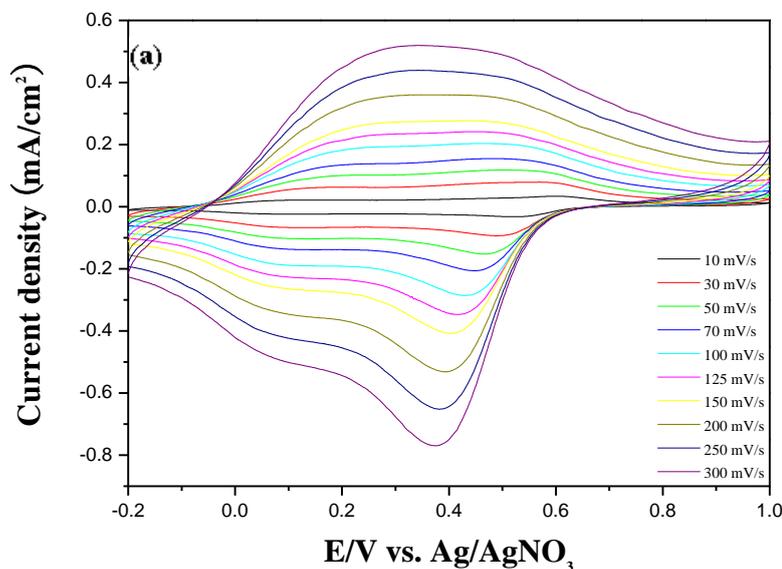


Figure 3. XPS spectra of (a) the survey scan for the PANI-PSS and PANI-HCl, and (b) the N_{1s} core-level of PANI-PSS.

Fig. 4 shows the electrochemical behavior of the PANI-PSS film at different scan rates between 10 and 300 mV/s in PC+LiClO₄ solution. As can be seen from Fig. 4a, the PANI-PSS film is cycled repeatedly between oxidized and reduced states without significant decomposition. The PANI-PSS film exhibited a reversible redox process at 0.30~0.42 V. The peak current densities (j) are proportional to the potential scan rates (Fig. 4b), indicating that the PANI-PSS film is electroactive and adheres well to the electrode [48]. In addition, anodic and cathodic peak currents reveal a linear relationship as a function of scan rate for the PANI-PSS, implying that the electrochemical processes of the PANI-PSS are reversible and are not diffusion limited [49].



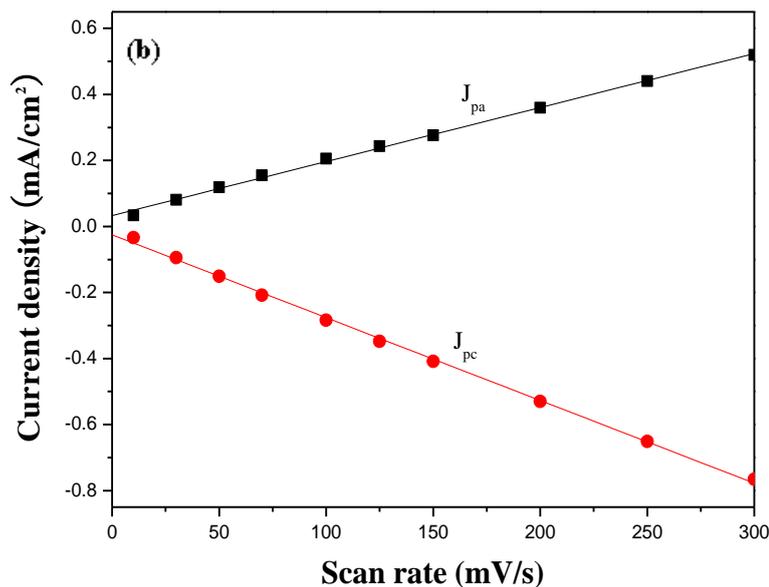


Figure 4. (a) CV curves of the PANI-PSS film at different scan rates between 10 and 300 mV/s in the LiClO₄ + PC solution. (b) Scan rate dependence of the PANI-PSS. J_{pa} and J_{pc} denote the anodic and cathodic peak current densities, respectively.

3.2. Spectroelectrochemical studies of PANI-PSS and PEDOT-PSS

One of the important means of studying the changes in the absorption spectra and characterizing the electronic structures of conjugated polymers is spectroelectrochemistry.

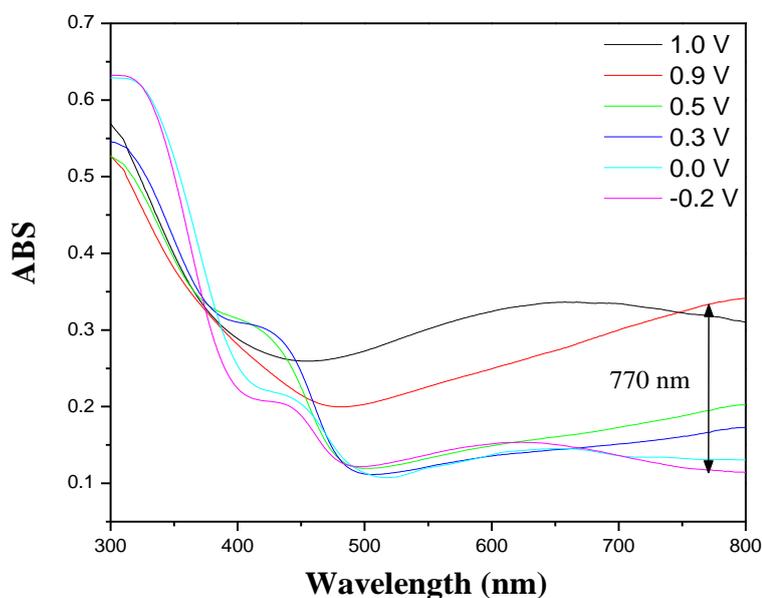


Figure 5. UV-visible spectra of PANI doped with PSS recorded from -0.2 V to 1.0 V.

response, the response times of the devices at 2, 600, and 1200 cycles were summarized in Table 2. For device (a), the response time was found to be 11.2 s from the bleaching state to the coloring state and 7.8 s from the coloring state to the bleaching state at 2 cycles. However, the response time was found to be 25.2 s from the bleaching state to the coloring state and 24.1 s from the coloring state to the bleaching state at 1200 cycles, implying the liquid state electrolyte in device (a) prolongs the response time significantly at long term cycles.

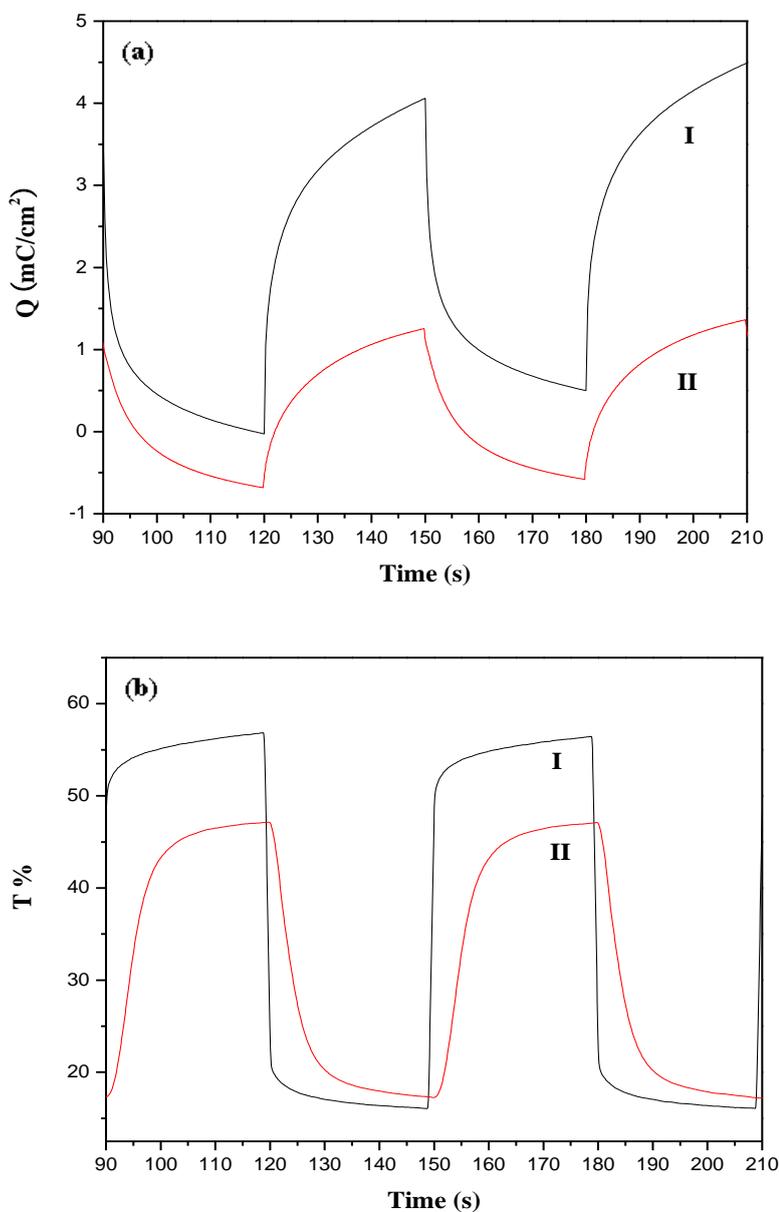


Figure 7. (a) Charge–time and (b) transmittance–time profiles of the ITO|PANI-PSS||PC-LiClO₄||PEDOT-PSS|ITO (I) and ITO|PANI-PSS||PMMA-PC-LiClO₄||PEDOT-PSS|ITO (II) devices in the range of -0.5 to 2.5 V for every 30 s.

On the other hand, the response time for device (b) was found to be 17.1 s from the bleaching state to the coloring state and 12.1 s from the coloring state to the bleaching state at 2 cycles, and 23.1 s from the bleaching state to the coloring state and 23.4 s from the coloring state to the bleaching state at 1200 cycles. Compare the response time of device (a) and device (b) at 1200 cycles, device (b) shows faster response time than device (a), indicating PMMA-base gel state electrolyte in electrochromic device prevent the prolongation of response time after long term cycles.

Table 2. Optical and electrochemical properties investigated at the selected wavelength (640 nm) for the devices.

	N	T _{ox}	T _{red}	ΔT	ΔOD	Q _d (mC/cm ²)	CE (cm ² /C)	τ _{c-b} (s)	τ _{b-c} (s)
Device (a)	2	16.2	57.3	41.1	-0.55	-3.98	138	7.8	11.2
	600	20.0	36.4	16.4	-0.26	-1.72	151	23.7	25.1
	1200	23.2	30.7	7.5	-0.12	-0.97	125	24.1	25.2
Device (b)	2	17.3	47.1	29.8	-0.44	-1.87	233	12.1	17.1
	600	23.1	47.2	24.1	-0.31	-1.26	246	20.4	21.8
	1200	28.4	44.3	15.9	-0.19	-1.10	175	23.4	23.1

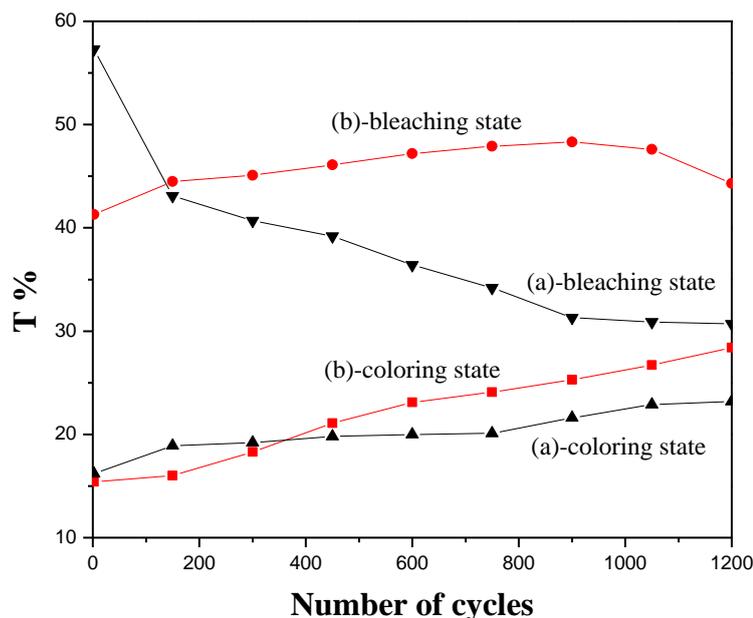


Figure 8. The cycling stability of (a) ITO|PANI-PSS||PC-LiClO₄||PEDOT-PSS|ITO (black line) and (b) ITO|PANI-PSS||PMMA-PC-LiClO₄||PEDOT-PSS|ITO (red line) devices at coloring state and bleaching state by switching the potential in the range of -0.5 to 2.5 V for every 30 s.

Another important characteristic of electrochromic materials is the optical contrast (ΔT %), which can be defined as the transmittance difference between the redox states, the optical contrast (ΔT %) at 640 nm was monitored, the ΔT % of the device (a) and device (b) were calculated to be 41.4 % and 29.8 % at 640 nm at 2 cycles, respectively, as shown in Table 2 and Fig. 8. However, the ΔT % of the device (a) and device (b) were 7.5 % and 15.9 % at 640 nm at 1200 cycles, respectively, demonstrating the incorporation of PMMA-based electrolyte in electrochromic device has larger ΔT % than that of liquid electrolyte after long term cycles.

Coloration efficiency (η) measurements provide a good guide for understanding the electrochromic characteristics. Coloration efficiency (η) is defined as the relationship between the injected/ejected charge as a function of electrode area (Q_d) and the charge in optical density, ΔOD , at a specific wavelength (λ_{\max}) as illustrated by the following equations [50,52]:

$$\eta = \frac{\Delta OD}{Q_d} \quad (3)$$

$$\Delta OD = \log\left(\frac{T_{\text{ox}}}{T_{\text{red}}}\right) \quad (4)$$

where T_{ox} is the transmittance of the oxidized state (coloring state); T_{red} is the transmittance of the reduction state (bleaching state). ΔOD is -0.55 and -0.44 for device (a) and device (b) at 2 cycles, respectively. However, ΔOD is -0.12 and -0.19 for device (a) and device (b) at 1200 cycles, respectively. Moreover, CE of device (a) and device (b) were measured as 151 cm²/C and 246 cm²/C at 640 nm after 600 cycles, which had reasonable coloration efficiency. Compare the electrochromic switching of device (a) and device (b), device (b) shows higher CE than device (a) after 2, 600, and 1200 cycles, indicating the incorporation of PMMA-based electrolyte in electrochromic device increases CE significantly.

4. CONCLUSIONS

Electrochromic device were assembled with configurations of ITO|PANI-PSS||PC-LiClO₄||PEDOT-PSS|ITO and ITO|PANI-PSS||PMMA-PC-LiClO₄||PEDOT-PSS|ITO, and characterized for their performances. Electrochromic switching study shows that optical contrast (ΔT %) and response time of electrochromic device based on PMMA-based gel electrolyte are 15.9 % and 23 s at 640 nm at 1200 cycles, respectively. CE of electrochromic device based on PMMA-based gel electrolyte is measured as 246 cm²/C at 640 nm at 600 cycles, which has satisfactory coloration efficiency. These studies demonstrate that electrochromic device based on PMMA-based gel electrolyte show good cycling stability and the PMMA-based gel state electrolyte is a candidate to replace liquid electrolyte in electrochromic device.

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