

Photoelectric Properties and Driving Characteristics of Prussian-blue-based Polymer Gel Electrochromic Cells

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ABSTRACT

The effects of polymer gel electrolyte on the photoelectric and driving characteristics in voltage of ± 1.5 V of Prussian Blue (PB)-based electrochromic (EC) cells were systematically investigated under preparation conditions of different electrolyte concentration and filmforming speed.

1 INTRODUCTION

Thin displays that are currently in widespread include "liquid crystal display" and "organic EL display". These displays are called "transmissive display" or "light emitting display" and function as full-color displays by controlling the three primary colors of red, green, and blue light. On the other hand, there is a display called "reflective display". This display uses light from the outside to display and images by reflecting external light sources such as the sun and fluorescent lamps on the display surface. It doesn't require a backlight or light emitting layer, and it is possible to continue displaying the image even after the voltage application is released (memory function). Therefore, this display is excellent in power consumption and thinning. In addition, it expected to develop as a next-generation display device such as color electronic paper. However, there is a problem that it is difficult to realize colorization.

In this study, we examine electrochromism (EC) that is increasingly used for light control glass. Specifically, EC is a reaction in which color is changed by voltage application, and subsequently it keeps the change without maintaining applied voltage. The EC material that is generally being

researched is tungsten oxide. Although it has good coloring efficiency and response speed, it has the disadvantages of being extremely expensive and the cost of the film forming process being enormous. We focus on Prussian Blue (PB) that corresponds to a low coat material wherein it is easy to prepare the film and it can be driven with low voltage. A low voltage drivable EC cell is shown in Fig. 1. Specifically, PB and nickel hexacyanoferrate (Ni-PBA) are coated on the transparent electrode, and an electrolyte layer containing K^+ is formed between the two transparent electrodes. When a voltage is applied, electrons and cations generated from the substrate and electrolytic solution move in and out of the PB film and Ni-PBA film when a voltage is applied, and the color changes due to the redox reaction of the metal ions in the film.

The crystal structures of PB and Ni-PBA fabricated via structure visualization software VESTA are shown in Fig. 2. PB and Ni-PBA have similar crystal structures. The crystal structure of PB is cubic and is crosslinked with $Fe^{2+}-CN-Fe^{3+}$. Specifically, PB exhibits a $Fe(II)(CN)_6$ missing in the unit lattice, and an insoluble PB is prepared. The crystal easily captures K^+ due to the neutral charge. Therefore, an electrolyte containing K^+ is adopted as the electrolyte layer of the EC cell. We fabricated PB-based EC cells and systematically examined the effect of film forming conditions and electrolytic solution concentration on electric characteristics and driving characteristics. A normal electrolyte was prepared, and a polymer gel electrolyte

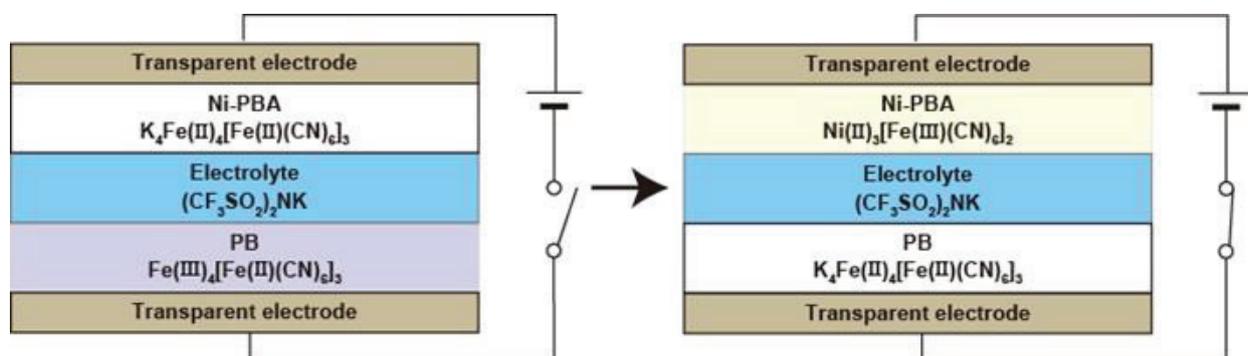


Fig. 1 Cell structures and chemical reactions of the PB-based EC cell

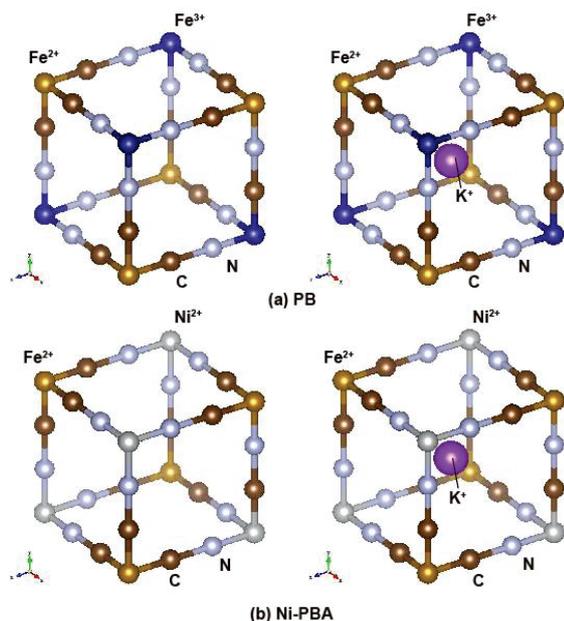


Fig. 2 Crystalline structures of (a) PB and (b) Ni-PBA

was prepared to further reduce the risk of leakage. We systematically investigated the effect of each on the characteristics.

2 EXPERIMENT

PB was purchased from Kanto Chemical Co., Tokyo, Japan, and prepared by mixing 9 wt% of FeHCF nanoparticles in water. Additionally, Ni-PBA was purchased from Kanto Chemical Co., Tokyo, Japan, and prepared by mixing 8 wt% of NiHCF nanoparticles into the water. Potassium bis(trifluoromethanesulfonyl) imide (Kanto Chemical Co., Tokyo, Japan) was used as the electrolyte.

While preparing the EC cell in Fig. 1, “8 different production conditions” are examined. The ITO substrate was cleaned with alcohol and subjected to hydrophilic treatment by plasma for approximately 1 min. Subsequently, PB films were formed at 1500 rpm or 7500 rpm for 20 s via the spin coating method using MS-A 100 spin coater (Mikasa Co., Ltd., Tokyo Japan). All Ni-PBA films were formed at 1500 rpm for 20 s. Potassium bis-(trifluoromethanesulfonyl)-imide ((CF₃SO₂)₂NK) exhibiting a concentration of 0.1 mol/L or 0.5 mol/L was dissolved in propylene carbonate. The ITO substrates with the PB film and with the Ni-PBA film were adhered at intervals of 100 μm. Additionally, an electrolyte layer was formed. The gel electrolyte was prepared by mixing 30 wt% of PMMA in the electrolyte prepared earlier at 95 °C for 24 h. The thickness of the Ni-PBA film of all the EC cells was maintained as constant. Additionally, EC cells with the thick PB film and the thin PB film were prepared. Furthermore, EC cells with high electrolyte concentration and with low electrolyte concentration were prepared. Moreover, EC cells using electrolyte and using a gel electrolyte were prepared. Moreover, EC cells using electrolyte and using a gel electrolyte were prepared. A total of eight types of EC cells were prepared. The preparation conditions are summarized in Table 1.

The impedance at each frequency of the eight types of EC cells was measured via a chemical impedance analyzer (IM 3590, Hioki E. E. Co., Nagano, Japan). Measurement was performed in the range of 0.1 Hz to 200 kHz. The applied voltage was set as 1 V to avoid deterioration of the EC cell under measurement.

3 RESULTS and DISCUSSION

3.1 Changes in appearance of EC cells

Specifically, in EC cell No.1, the PB film was formed

Table 1 Preparation conditions of the EC cell

Cell No.	Spin-coating speed (rpm)	Electrolytes	Electrolyte concentration (mol/L)
1	1500	Electrolyte	0.1
2	1500	Electrolyte	0.5
3	7500	Electrolyte	0.1
4	7500	Electrolyte	0.5
5	1500	Gel-Electrolyte	0.1
6	1500	Gel-Electrolyte	0.5
7	7500	Gel-Electrolyte	0.1
8	7500	Gel-Electrolyte	0.5

at 1500 rpm. The electrolyte concentration corresponded to 0.1 mol/L. In EC cell No.4, the PB film was formed at 7500 rpm. The electrolyte concentration corresponded to 0.5 mol/L. In EC cell No.5, the PB film was formed at 1500 rpm. The gel electrolyte concentration corresponded to 0.1 mol/L. In EC cell No.8, the PB film was formed at 7500 rpm. The gel electrolyte concentration corresponded to 0.5 mol/L.

Fig. 3 displays the photographs depicting the changes in appearance as the EC cells are driven at ± 1.5 V. With respect to the applied voltage of 1.5 V, decoloring at the cathode due to injection of electrons into the PB film was observed in all the EC cells. With respect to the applied voltage of -1.5 V, coloring at the cathode due to the oxidation of the PB film was observed in all the EC cells. The decoloring was unclear in EC cells Nos. 1 and 5. In EC cells Nos. 4 and 8 with a thin PB film, decoloring was evident in all cases. EC cells Nos. 1 and 5, and Nos. 4 and 8 display approximately the same degree of sharpness of decoloring. Gelling did not affect the appearance.

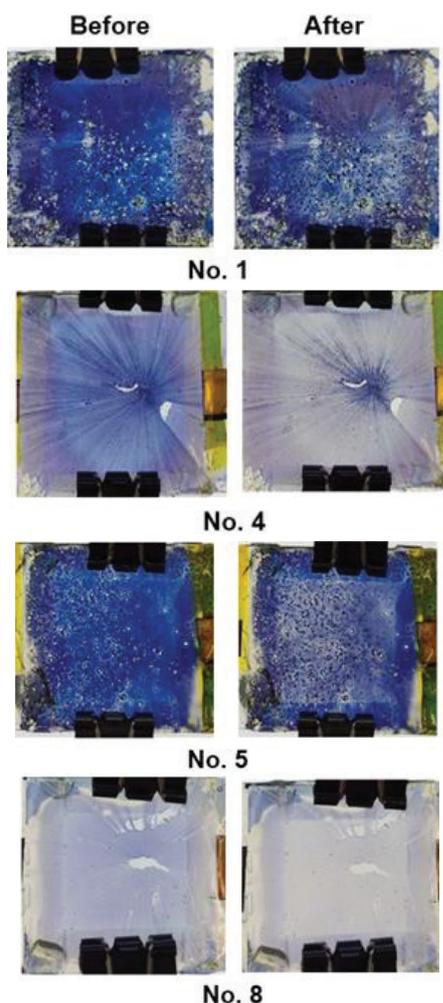


Fig. 3 Switching images of EC cells with the application of DC voltage of ± 1.5 V

3.2 Measured response times of EC cells

We fabricated the electronic circuit and conducted the experiment of driving the EC cell. In contrast to the driving circuit of the inorganic EL of the previous report, we fabricated the simply ON/OFF switching circuit [1].

Measurement of responsiveness of the EC cell was performed by measuring the difference in light transmittance due to the color change that occurred with respect to the application of ± 1.5 V every 3 s as the voltage value of the photodiode as in the previous report [2]. Fig.4 shows the photodiode output signal with respect to the application of ± 1.5 V switched every 3 s. The results for EC cells Nos. 1, 4, 5, and 8 are shown as a representative result. In EC cell No.1 (Fig. 4(a)), the PB film was formed at 1500 rpm. The electrolyte concentration corresponded to 0.1 mol/L. In EC cell No.4 (Fig. 4(b)), the PB film was formed at 7500 rpm. The electrolyte concentration corresponded to 0.5 mol/L. In EC cell No.5 (Fig. 4(c)), the PB film was formed at 1500 rpm. The gel electrolyte concentration corresponded to 0.1 mol/L. In EC cell No.8 (Fig. 4(d)), the PB film was formed at 7500 rpm. The gel electrolyte concentration corresponded to 0.5 mol/L.

In all EC cells, a reversible change was observed in which the voltage value of the photodiode increased after the voltage was turned on and decreased after the voltage was turned off. However, the trend was different for each EC cell. As shown in the results of the electrical properties and chemical reactivity, the voltage value gradually increased in EC cell No. 1 (which is expected to affect the progress of the reaction slightly) and the voltage exhibited a tendency to gradually decrease after

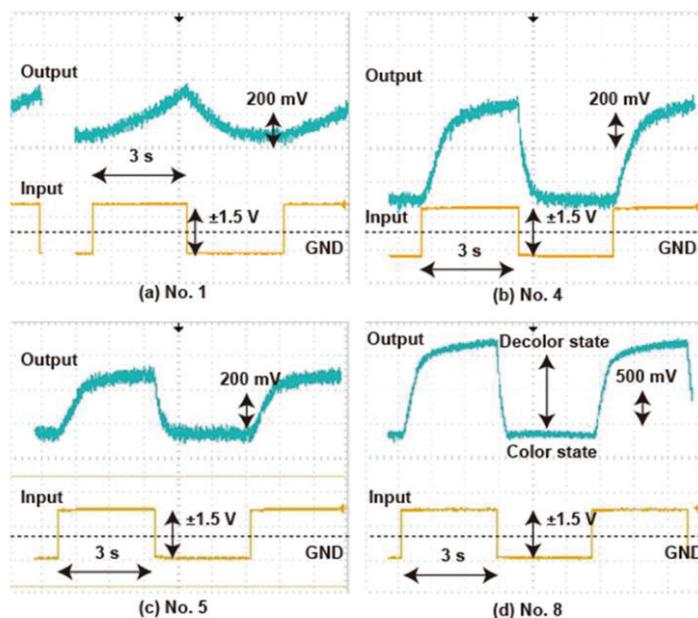


Fig. 4 Measured response times in the EC cells

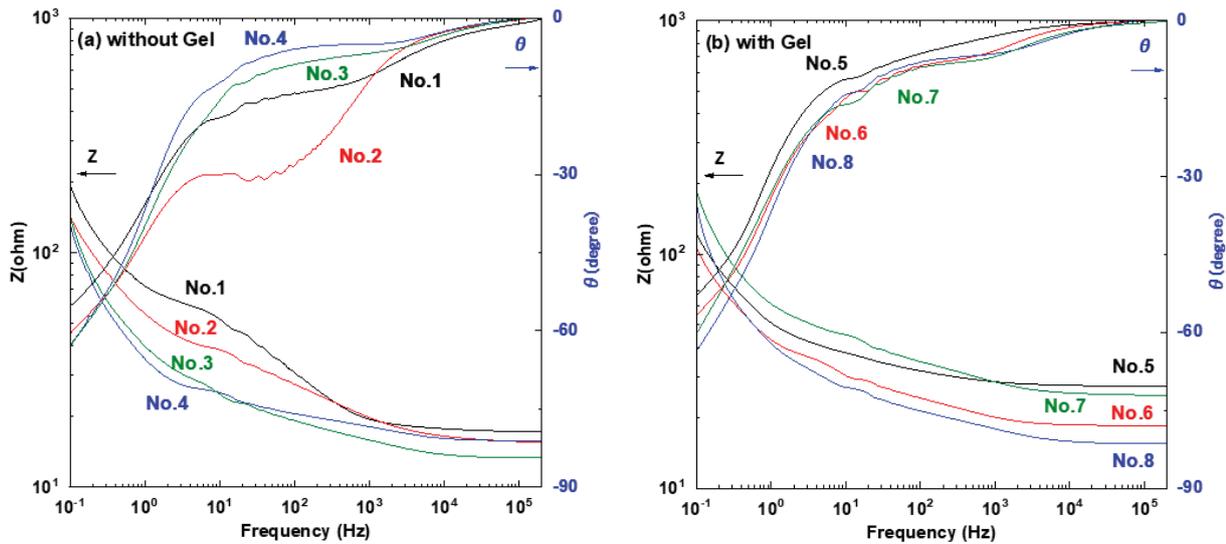


Fig. 5 Impedance and phase of the EC cells

it turned OFF. Conversely, the chemical reactivity was expected to become faster in No. 4 where the thickness of the PB film was small and electrolyte concentration was high. The change sharply increased in the range of approximately 1 s immediately after the voltage application, and then it exhibited a two-step behavior that gradually increased while reaching the steady state until it turned OFF. The change sharply decreased in the range of approximately 1 s immediately after it turned OFF and exhibited a two-step behavior that gradually decreased while it reached the steady state until it turned ON. Evidently, the reactivity increased by thinning the PB film and increasing the electrolyte concentration.

3.3 Impedance and phase of EC cells

With respect to the frequency dependence of the impedance (Z) and phase (θ) of the EC cell, the result of the EC cell with the electrolyte is shown in Fig. 5(a), and the result of the EC cell with the gel electrolyte is shown in Fig. 5(b). The impedance Z of the EC cell corresponded to 132–195 Ω in the low frequency region of EC cells Nos. 1–4. Specifically, Z decreased when the thickness of the PB layer reduced and the electrolyte concentration increased. With respect to Nos. 1 and 2, where the PB film was thick, it slowly decreased once around 10 Hz and subsequently decreased with increases in the frequency. In the high frequency region, the value converged to 17.2 Ω , 15.4 Ω , 15.7 Ω , and 13.3 Ω for EC cell Nos. 1, 2, 3, and 4, respectively. In EC cells, using the gel electrolyte, Z approximately corresponded to 105–185 Ω in the low frequency region. Additionally, the value of Z converged to 27.2 Ω , 18.5 Ω , 24.9 Ω , and 15.5 Ω for EC cell Nos. 5, 6, 7, and 8, respectively.

The phase θ due to the resistance and capacitance components of the EC cell was -56° – -63° in the low frequency region of EC cell Nos. 1–4, and the capacitance

component was strong. However, in the high frequency region, it converged to 0° and shifted to the resistance component. For EC cell Nos. 1 and 2, the shift was moderate at approximately 10 Hz. Conversely, EC cell Nos. 5–8 using the gel electrolyte, a shift from the capacitance component to the resistance component was observed.

Their trajectories were almost identical, and the component as the element was stable without depending on the preparation conditions.

4 CONCLUSIONS

We prepared several types of PB-based EC cells and an automatic driving circuit. Additionally, the effect of polymer gel electrolyte on the electrical properties and driving characteristics of the EC cells was systematically investigated. The thickness of PB layer significantly depended on their switching speed as opposed to the electrolyte concentration and polymer gel electrolyte. However, it was easy to observe the switch from coloring to decoloring state for the gelation of the electrolyte.

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