

Letter

Electrochromic Stability of Polypyrrole Films on ITO Electrode Modified with Au Nano-islands

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Abstract: Island-shaped Au nano-particles were immobilized on an ITO transparent conductive film by a pulse electrolysis method capable of controlling the nucleation and the nuclear growth. Using this as an electrode, a polypyrrole thin film was immobilized by electrochemical polymerization. It was confirmed that the electrochromic stability of the polypyrrole film was greatly improved on the ITO electrode modified with the Au nano-islands.

Key words: ITO electrode modified with Au nano-islands, Polypyrrole, Electrochromic stability

In the study of electrochromic (EC) displays using conductive polymers, improving the responsiveness and stability of the color changes associated with the electrochemical redox reaction is the most important subject for their practical application. Nevertheless, there are not many direct studies for improving the stability of the EC changes. On the other hand, in the research of secondary batteries, the stability of the charge and discharge has been very actively studied. The EC device and a battery are common in that they undergo a redox reaction at the electrode. For the redox reaction of the conductive polymer film, ion doping and dedoping occur, and the expansion and shrinking of the polymer chain as a result of the formation of the π -conjugated system causes a large and powerful volumetric change in the film. After repeated redox reactions, mechanical stress due to the volumetric changes will accumulate in the polymer film near the electrode surface.^{1,2)} This causes peeling of the polymer film from the electrodes, resulting in a decrease in the electrochemical activity of the entire film and the amount of the EC color changes. In recent research on batteries, a method of strengthening the polymer stacking by forming nano-sized structures on the electrode surface has been often utilized for improving its stability.^{3,4)} This method not only enhances the stability, but also expands the effective area of the electrode and simultaneously improves the storage capacity.

Improving the EC stability of polypyrrole (PPy) was achieved using the Au nano-rod array electrodes in our previous study.⁵⁾ It was considered that this method not only improved the stacking of the polymer film, but also suppressed the peeling from the electrode by the soft Au nano-rods following the expansion and shrinking of the polymer film due to the redox reaction. The nano-structures with a Au rod array were obtained by the template method, and the polycarbonate porous membrane and alumina porous plate used as the template were commercial products and very expensive, and the nano-rod diameters and the number of rods were predetermined. In

order to overcome these inconveniences, a new approach was employed to form nano-structures without templates. For the method of forming Au nano-particles on the surface of a ITO electrode by pulse electrolysis, the size and number of particles can be freely controlled.^{6,7)} By using this new ITO electrode obtained by this method, the electrochemical polymerization of pyrrole would be induced at a lower applied potential than that when a normal ITO electrode was used. Furthermore, it was found that the deterioration of the polymer during the polymerization was suppressed by using the new ITO electrode.⁸⁾ In this study, using the island-shaped Au nano-particles immobilized ITO electrode, the stability of the change in transmittance of the PPy film due to EC was evaluated and compared to the normal ITO electrode.

The electrolyte solution for forming Au nano-particles on the ITO electrode was prepared as an aqueous solution containing 100 mM potassium sulfite and 30 mM Au (I) sodium sulfite in ultrapure water. An electrolysis device was fabricated by sandwiching the electrolyte solution between two glass electrodes with ITO thin films (manufactured by Geomatec) via a silicon O-ring (effective area: 2 cm²). As an example of the electrolysis conditions, a DC voltage of -10 V was applied to the device for a short time (several ms) to deposit Au nuclei on the electrodes, then a DC voltage of -1.1 V was applied for 60 s to grow the Au nuclei. The obtained Au-ITO electrodes were washed with ultrapure water, and then dried in air.

An aqueous solution for the polymerization containing 10 mM pyrrole and 0.1 M lithium perchlorate was placed in a transparent glass cell as the container, and silver chloride was immersed as a reference electrode, platinum wire was immersed as a counter electrode, and Au-ITO electrodes were the working electrode. To immobilize the PPy film on the electrode, a potential scanning polymerization was carried out at the rate of 50 mV/s in the range of -500

mV to +1000 mV (vs. Ag-AgCl).

For evaluation of the EC stability of the PPy film, the time dependence of the transmittance of the entire electrolytic cell were measured at a wavelength of 700 nm to the light incident from the tungsten light source using an electrolyte solution containing 0.1 M lithium perchlorate. The resulting transmittance value of 100%, therefore, included the entire absorption of the glass cell, the electrolyte solution, and the ITO electrode.

Since the Au-ITO electrode obtained by pulse electrolysis had an absorption maximum at the wavelength of 580 nm (transmittance of 67%) based on plasmon scattering, the diameter of the formed island-shaped Au nano-particles was expected to be about 60 nm.⁷⁾

When constant potentials of -400 mV and +800 mV were applied to the PPy films on the electrode in an aqueous solution containing lithium perchlorate, color changes were observed due to their electrochromism. The PPy films (film thickness: 100 nm for ITO and 150 nm for Au-ITO) formed by potential scanning polymerization of 20 cycles on both electrodes showed a change in the transmission spectrum as shown in Fig.1. A change in transmittance in the visible long wavelength region based on the $\pi-\pi^*$ transition of the PPy was observed during the switching between the oxidized and reduced states. In the case of the normal ITO electrode, the transmittance decreased to about 80% at the wavelength of 700 nm after 20 cycles of polymerization, and a 9.0% electrochromic change in the transmittance was obtained between both redox states. In the case of the Au-ITO electrode, plasmon scattering of the Au nano-particles immobilized on the ITO surface probably included to the absorption of the ITO electrode. Therefore, the transmittance of the Au-ITO electrode decreased to about 50% at a wavelength of 700 nm after 20 cycles of polymerization, and a 25.0% electrochromic change in transmittance was obtained between both redox states. Since the thickness of the PPy film on the ITO electrode was around 100 nm, and on the Au-ITO electrode, it was around 150 nm, it is considered that the amount of EC change in transmittance

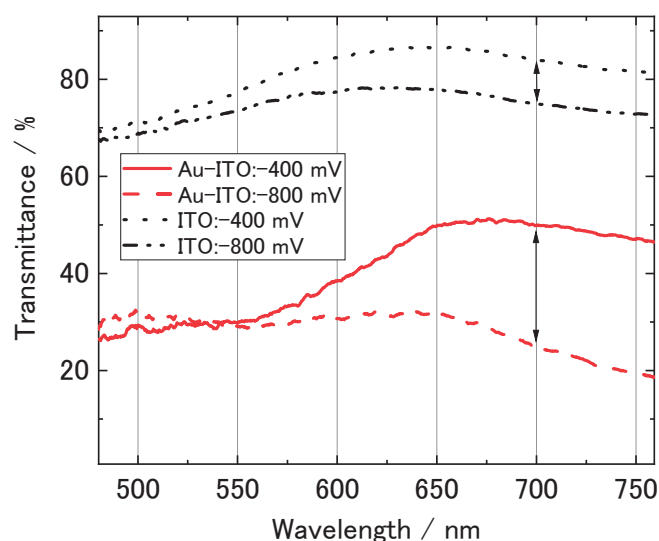


Figure1 Transmittance spectra of the PPy films (20 cycles polym.) on the ITO and the Au-ITO in the redox states at the applied potentials of -400 mV and +800 mV.

(ΔT) was mainly due to the difference in the film thickness.

Using the same sample as in Fig. 1, the time dependence of the transmittance at a wavelength of 700 nm was measured when cyclic scanning was performed between the applied potentials of -400 mV and +800 mV at the rate of 50 mV/s. The results of the comparison between the normal ITO electrode and the Au-ITO electrode are shown in Fig. 2. With the ITO electrode, the change in transmittance, which was initially 9.0% (ΔT_1), decreased to 2.2% (ΔT_{20}) after 20 redox cycles. On the other hand, with the Au-ITO electrode, the change in transmittance, which was initially 25.0%, decreased to 13.4% after 20 redox cycles.

The decay of ΔT was evaluated as the ratio of ΔT_{20} to ΔT_1 , [Decay of $\Delta T = ((\Delta T_{20}) / (\Delta T_1)) \times 100$] to be 25.0% for the ITO electrode and 54% for the Au-ITO electrode. The decay was significantly suppressed by using the Au-ITO electrodes, thus resulting in an improved stability.

The decay process of the ΔT was discussed for the PPy film thickness in the latter half. Figure 3 shows the results of comparing the relationship between the decay and the number of redox cycles at each electrode by the number of polymerization cycles of PPy. On the ITO electrode, the film thickness was about 100 nm after 20 polymerization cycles, and about 150 nm at the 40th cycle. On the other hand, on the Au-ITO electrode, the PPy film thickness was about 150 nm after 20 polymerization cycles, and about 200 nm at the 40th cycle. For both electrodes, the PPy film thickness tended to increase as the polymerization cycle increased. The PPy film thickness on the Au-ITO electrode was thicker than that on the ITO even for the same polymerization cycles. This suggested that the Au nano-particles can promote the deposition of the PPy polymer.⁸⁾ The Au nano-particles obtained on the ITO electrode were slightly flattened in the plane direction, so it could not be simply determined, but it was one of the factors affecting the increase in the film thickness of the PPy obtained on the Au-ITO electrode. As shown in Fig.3, the decay of ΔT progressed as the number of redox

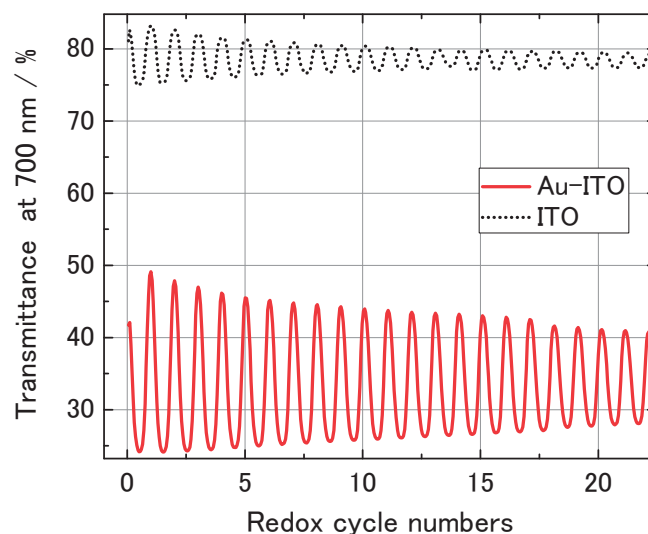


Figure 2 Time dependences on the transmittance of PPy films (20 cycles polym.) on the ITO electrode and the Au-ITO electrode at the wavelength of 700 nm during the applied potential cycling between -400 mV and +800 mV.

cycles increased on both electrodes. The large difference between the two electrodes was that a rapid drop was found on the ITO electrode during the initial stage. During the subsequent stage, however, the two decays seemed to have almost the same slope on both electrodes. It is considered that the decay in the subsequent stage is due to the reason that an aqueous solution is used as the electrolyte solution, so that the hydrolysis of PPy occurs due to peroxidation, and the electrochemical activity is gradually deteriorated. The rapid drop in the initial stage of the ITO electrode suggested that the volume of the PPy film changes with the redox reaction, and the PPy film is peeled off from the electrode. In fact, in the ITO electrode, it was confirmed that the PPy film was peeled off when the electrode was removed from the electrolytic cell after the experiment. Regarding the difference in the PPy film thickness, the initial decay occurred on both electrodes, but the steeper decay was

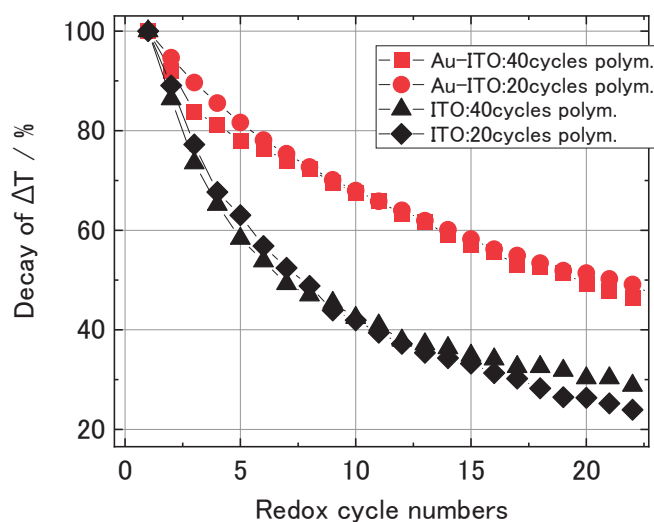


Figure 3 Electrochromic stabilities of the PPy films on the ITO electrode and the Au-ITO electrode for 22 applied potential cycles between -400 mV and $+800$ mV at the scan rate of 50 mV/s. The decay of ΔT was calculated from $[\text{Decay of } \Delta T = ((\Delta T_{20}) / (\Delta T_1)) \times 100]$.

found from the thicker PPy film. The volumetric change of the PPy film associated with the redox reaction must be greater on the electrolyte solution side than on the electrode substrate side. Because the freedom of movement is limited on the electrode substrate side, the mechanical stress of the PPy film is enhanced by the continuous redox reaction. It is considered that this tendency becomes stronger as the film thickness increases.

An aqueous electrolyte solution was used in the study so that the decay of the EC change of PPy strongly took place on both electrodes by hydrolysis due to peroxidation. However, the stacking between the electrode and PPy film was strengthened by using the Au-ITO electrode, which had nano-structures consisting of Au nano-particles. This can suppress peeling of the PPy film due to the redox reaction, and the stability of the EC changes would be finally improved.

In the future, the EC stability of the PPy film will be evaluated by focusing more on the effect of the volumetric change of the film under conditions when the hydrolysis is suppressed by using a non-aqueous solution for the polymerization and the EC experiments.

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