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Spectroelectrochemical Properties of Phenolphthalein Incorporated within a Poly(Hydroquinone/p-Benzoquinone) Film

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Electrochemical oxidation-reduction of poly(mercaptohydroquinone/mercapto-p-benzoquinone) causes a rapid and large pH change in the polymer film in an aqueous solution. Phenolphthalein, a typical pH indicator, incorporated within the polymer film on a SnO_2 electrode showed a rapid reversible color change from red to colorless when the electrode potential is repetitively stepped between -0.6 (reduction) and +0.4 V vs. SCE (oxidation).

There has been a continuous interest over the last several years to examine the transition metal oxides,[1-3] the electrochromic active sites incorporated within polymers,[4-6] the conductive polymers prepared by electropolymerization,[7-9] and the others[10, 11] as the basis for electrochromic displays. All spectroelectrochemical behavior observed of these materials are directly based on the coloration of their electrochemically reduced or oxidized forms.

Recently we have reported the preparation of poly(mercaptohydroquinone/mercapto-p-benzoquinone) film (SQE_{Red}/SQE_{Ox}) by means of an electrochemical polymerization of mercaptohydroquinone.[12, 13] The polymer film thus prepared is stable and shows no change in the shape of the cyclic voltammogram after more than 1000 times repetitive potential scanning from +0.7 V vs. a saturated calomel electrode (SCE) to H_2 evolution potential. In addition, both SQE_{Red} and SQE_{Ox} are almost colorless, transparent films. The reduction-oxidation equilibrium between SQE_{Red} and SQE_{Ox} can be represented by $SQE_{Red} \rightleftharpoons SQE_{Ox} + nH^+ + ne$, where n equals 2 per one hydroquinone unit in SQE_{Red}. The electroreduction of SQE_{Ox} in an aqueous solution increases the pH value in the polymer film, and the electrooxidation of SQE_{Red} decreases the pH value. This will bring about a reversible, visible color change if a pH indicator is incorporated in the polymer film (Fig. 1).

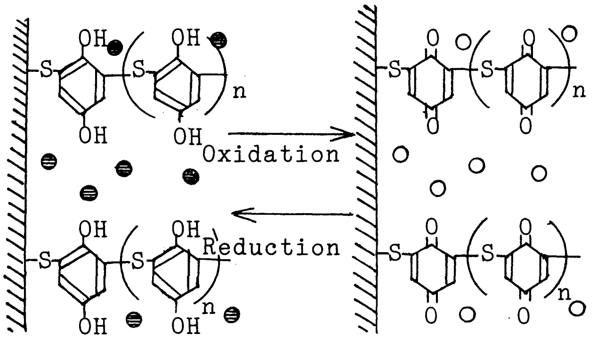

Fig. 1. Scheme of electrochromism using phenolphthalein(PP) incorporated within poly (mercaptohydroquinone/ mercapto-p-benzoquinone) film.

● : Colored PP.

○ : Discolored PP.

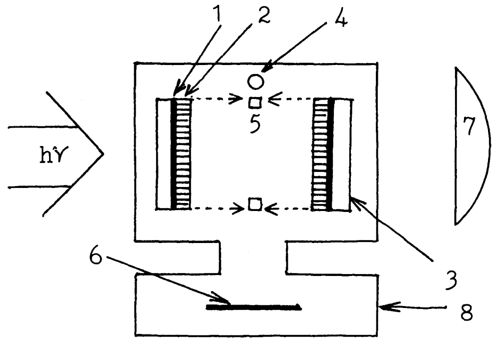

Fig. 2. Schematic view of the experimental arrangement for transmission spectroelectrochemical measurements.

1 : SnO_2, 2 : PP-impregnated polymer, 3 : Substrate glass, 4 : Salt bridge, 5 : Silicon rubber, 6 : Counter electrode, 7 : Detector, 8 : H-type glass cell.

We report here spectroelectrochemical properties of phenolphthalein (PP), a typical pH indicator, which is incorporated within an SQE_{Ox}/SQE_{Red} film. The quinone-form film was prepared on a SnO_2 electrode by the electrochemical polymerization of mercaptohydroquinone (1 mM, 1 M = 1 mol dm^{-3}) at a constant potential of +0.7 V vs. SCE for 6 h in a Britton-Robinson buffer solution having pH 7.0 containing 20 % volume fraction ethanol at a room temperature in a nitrogen atmosphere, the other polymerization conditions being identical with those previously[12)] used on a glassy carbon electrode. The polymer-coated electrode showed a cathodic peak at ca. -0.5 and an anodic peak at ca. +0.3 V vs. SCE on the cyclic potential scanning from +0.7 to -0.8 V vs. SCE in the Britton-Robinson buffer solution having pH 7.0. The polymer-coated SnO_2 electrode thus prepared was washed repeatedly with water and then it was allowed to air dry at room temperature. An amount of ethanol solution containing 1 % mass fraction PP was spread over the polymer-coated SnO_2 surface, and then the solvent was allowed to evaporate.

The spectroelectrochemical properties of the resulting PP-impregnated electrode were examined with a three-electrode system consisting of a Pt wire counter electrode, an SCE reference electrode, and an electrochromic working electrode (ca. 1 cm^2 in effective area[14)). The electrochromic working electrode consisted of a pair of the PP-impregnated electrodes which were held together in face to face position with two silicon rubber spacers (ca. 0.5 mm in thickness) in between as shown in Fig. 2. A 0.1 M KCl aqueous solution was used for the cell supporting electrolyte solution and it's pH was adjusted to 7.5 by the addition of a small quantity of NaOH just before measurement. Spectroelectrochemical measurement was carried out with a spectrophotometer Shimazu UV-240, in which the cell equipped with the colored PP-impregnated SnO_2 working electrode, a Pt plate counter electrode, and an SCE as a reference electrode was mounted on a light path as shown in Fig. 2. Figure 3 shows an absorption spectrum of the colored PP-impregnated SnO_2 electrode when SQE_{Ox} was reduced at -0.6 V vs. SCE. The absorption maximum at 560 nm observed on the PP-impregnated SnO_2 electrode is obviously due to the coloration of PP in the polymer (see Fig. 3 inset). Figure 4 shows the changes of absorbance at 560 nm caused by the reduction and the oxidation of the PP-impregnated SnO_2 electrode when the electrode potential is stepped from -0.6 to +0.4 V and then from +0.4 to -0.6 V vs. SCE.

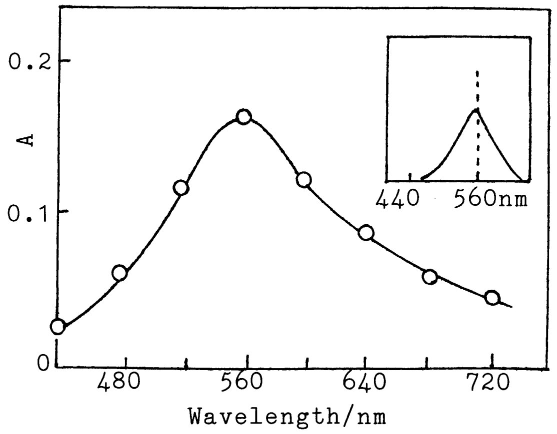

Fig. 3. Relationship between absorbance and wavelength of the transmitted light through the colored PP on SnO_2. Inset, the absorption spectrum of a colored PP alkaline solution.

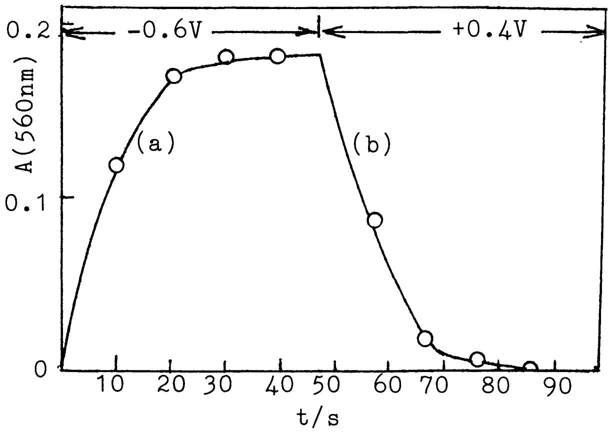

Fig. 4. The coloration(a) and discoloration(b) of the PP-impregnated polymer on SnO_2 induced by the alternate redox reaction of the polymer.

Neither oxidation nor reduction of PP was observed over the potential range -0.6 —— +0.4 V vs. SCE. This spectral change was easily observed visually: the electrode became red in a few seconds when reduced and colorless when oxidized after 20 repetitive potential steps.

Similar spectroelectrochemical behavior was observed on the polymer coated SnO_2 electrode where indooxime (IO), another pH indicator, was incorporated in the same manner. The IO-impregnated SnO_2 electrode changed it's color quickly from blue to red with the potential steps between the same potentials as above.

The present results show that a variety of colorations of the polymer-coated SnO_2 electrode may be accomplished by incorporating in the polymer film suitable pH indicators showing color changes over a pH range from 3 to 10.15)

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14) The effective area means the total area of the SnO_2 electrode surfaces modified with the PP-impregnated SQE_{Red} or SQE_{Ox}.

14) The pH range was estimated from the quantity of electricity required for the reduction and/or the oxidation of the polymer film in the electrochromic working electrode used here.

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