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ELECTROCHROMIC BEHAVIOR OF AMORPHOUS NICKELPHTHALOCYANINE THIN FILMS

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ABSTRACT

Amorphous nickelphthalocyanine (NiPc) thin films were prepared by vacuum evaporation and their electrochromic behavior and voltammograms were examined in the five kinds of aqueous electrolytes. Amorphous NiPc films were prepared on indium-tin-oxide (ITO) glass substrates cooled to -120°C by using liquid nitrogen under a vacuum of 2.4×10^{-4} Pa.

The voltammetric and electrochromic measurements were made using a potential galvanostat. In order to confirm the color change, optical vis-transmission spectra of the NiPc films were measured by a spectrophotometer with various electrode potential applied.

The NiPc amorphous thin films exhibited most clearly electrochromism in KNO_3 aqueous electrolyte. The specimen films underwent 3 color transitions (from blue to yellow-green, then to red violet, then to dark blue), corresponding to the three peaks on the voltammograms in KNO_3 aqueous electrolyte. Blue is color of the as-prepared film. When the potential was swept, charge compensation was attained upon oxidation by injection of anions from the electrolyte and upon reduction by expulsion of anions.

INTRODUCTION

Organic materials such as phthalocyanine and viologen, show electrochromism as well as inorganic materials^{1,2)}. Osada and Mizumoto reported that Copper-phthalocyanine (CuPc) films without pore channels prepared by plasma polymerization did not show electrochromism³⁾. Khono reported on the electrochromic behaviors of amorphous and polycrystalline CuPc vacuum evaporated thin films⁴⁾. It was confirmed that an electrochromic cell with an amorphous CuPc thin film in a LiClO_4 solution exhibited three different colors associated with changes in bias potentials. However, polycrystalline films did not show a color

change, except for a decrease in transmittance. Kato studied the electrochromic behavior of Zinc-phthalocyanine (ZnPc) and reported the difference of the phenomena between polycrystalline ZnPc and amorphous one in detail⁵⁾. Since the molecular configuration of amorphous films is assumed to be more random more porous than crystalline films, anions may be more easily diffused into amorphous films than into polycrystalline films. This promotes an electrochromic reaction in amorphous films which can be expected to clearly show electrochromism.

In this study, amorphous Nickelphthalocyanine (NiPc) thin films were prepared by vacuum evaporation, and their electrochromic

mic behavior and voltammograms were examined in five kinds of the aqueous electrolyte.

EXPERIMENTAL

Amorphous NiPc films were prepared on indium-tin-oxide (ITO) glass substrates by vacuum evaporation under a vacuum of 2.4×10^{-4} Pa. The temperature of the Mo boat (evaporation source) was kept between 410 °C during evaporation. In order to obtain amorphous films, the glass substrate was cooled to -120°C by using liquid nitrogen during vacuum evaporation. The evaporation rate was 0.05nm/s. The thickness of the NiPc films was typically 300nm. The structure of the NiPc films was examined by X-ray diffraction(XRD).

Electrochromic (EC) cells were fabricated from these NiPc films as follows. A lead wire was fitted to the edge of the ITO layer with silver conductive paint. The surface of the NiPc film was made insulating by silicone resin, exposed for the front face (10×10 nm), which was exposed to the electrolyte solution. The EC cell was mounted along the edge of the glass tube with silicone resin. Five elect-

rolytes were used in this study, namely KNO_3 , K_2SO_4 , KCl , NaCl , and MgCl_2 in 0.5M aqueous solutions.

The voltammetric and electrochromic measurements were made as shown Fig. 1 using a potentiogalvanostat and a potential sweeper in a simple cell with three electrodes. The NiPc working electrode (CE) and the saturated calomel reference electrode (RE), to which all potentials were referenced, were immersed in liquid electrolyte. The potential sweep rate was 33mV/s and the bias potential was changed from 0 to $\pm 1.5\text{V}$ for the voltammogram measurements. In order to confirm the color change, optical vis-transmission spectra of the NiPc films were measured by a spectrophotometer with various electrode potentials applied.

RESULTS AND DISCUSSION

Fig. 2 shows the X-ray diffraction pattern of a vacuum evaporated NiPc film. It shows that the amorphous film was obtained on the ITO glass substrate. Fig. 3 shows a typical cyclic voltammogram for NiPc in 0.5M KNO_3 . This was obtained by sweeping the bias po

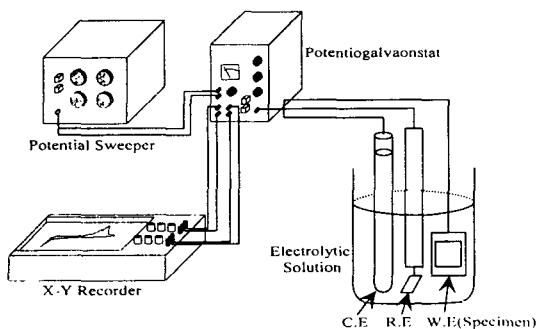


Fig. 1 Measurement apparatus for voltammograms.

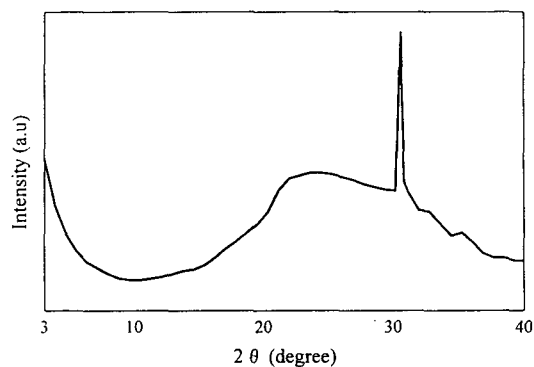


Fig. 2 X-ray diffraction of pattern of amorphous NiPc thin film.

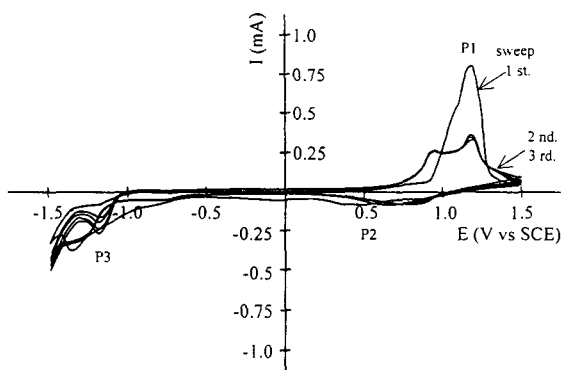


Fig. 3 Cyclic voltammogram for amorphous NiPc film 0.5M KNO_3 aqueous electrolyte.

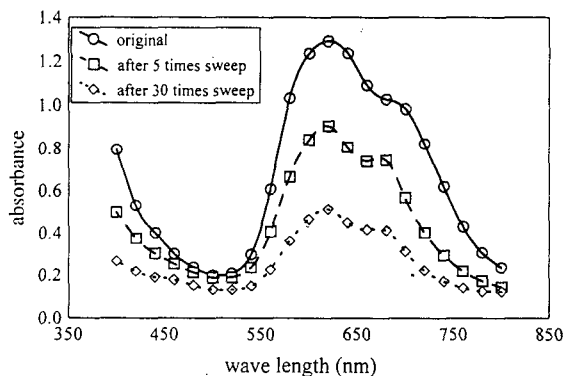


Fig. 4 Absorbance spectra for amorphous NiPc film after potential sweeping

tential at a scan rate of 33mV/s, starting from the rest potential R to +1.5V and then to -1.5V via 0V and finally back to the starting point. Corresponding to the peaks P1, P2, and P3 in the voltammogram, this specimen showed color transition visible to the needed eye as follows: blue to red-violet at peak P1, then to yellow-green at peak P2, and then to violet-blue at peak P3.

Fig. 4 shows the absorption spectra of the amorphous NiPc film after sweeping. "Original color" means that of the as-prepared film (blue). When the potential was swept, change compensation was attained upon oxi-

dation by injection of anions from the electrolyte at P1, and upon reduction by expulsion of anions at peaks P2 and P3.

For example, the presence of anions in oxidized ZnPc films has been confirmed by Auger electron spectroscopy⁶⁾. As the size of the anions limits their ability to enter the films, this limits the rate and the extent of film oxidation. Garvriov et al. reported that CoPc undergoes two oxidation processes, the first of which is quasi-reversible and the second is irreversible⁷⁾.

Also, Gavrilov et al. and Green et al. reported that the first oxidation takes place at the Pc ligand ring for both CoPc and ZnPc, and that the second oxidation for CoPc and ZnPc, and that the second oxidation at the center metal^{6, 7)}.

Also, when potential sweeping was repeated many times, bleaching of specimen films was confirmed in Fig. 4 to break. Especially absorbance of red color decreased. NiPc films showed clear electrochromism in KCl aqueous solution as well as KNO_3 solution but didn't show clear electrochromism in NaCl and MgCl aqueous solution.

CONCLUSION

Amorphous Nickelphthalocyanine thin films were deposited on indium-tin-oxide (ITO) glass substrates by means of a vacuum evaporation technique and their electrochromic properties were investigated in the five kinds of electrolytic solution. NiPc thin films exhibited clearly electrochromic behavior in 0.5M KNO_3 and KCl aqueous solution.

The specimen films underwent 3 color transition (from blue to yellow-green, then to red

violet, then to dark blue), corresponding to the three peaks on the voltammograms in KNO_3 aqueous electrolyte. Blue is color of the as-prepared film. When the potential was swept, charge compensation was attained upon oxidation by injection of anions from the electrolyte and upon reduction by expulsion of anions.

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REFERENCES

1. G. C. S. Collins and D.J. Schiffirin, J. Electroanal. Chem. **138**, 335 (1992).
2. C. J. Schoot, J. J. Ponjee, H. T. Van Dam, R. A. Van Dorn and P. T. Bolwijn, Appl. Phys. Lett. **23**, 64 (1973).
3. Y. Osada and A. Mizumoto, J. Appl. Phys. **59**, 1776 (1986).
4. Y. Khono, M. Masui, K. Ono, T. Wada and M. Takeuchi, Jpn. J. Appl. Phys. **3**, 252 (1992).
5. K. Kato, M. Masui, F. Kaneko, M. Takeuchi, T. IEE Japan **155-A**, 817 (1995).
6. J. C. Buchholz, Appl. Surf. Sci. **1**, 547 (1978).
7. V. I. Gavrilov, N. V. Butasova, E. A. Luk'yanets and I. V. Shellepin, Electrokhimiya **16**, 1661 (1980).
8. J. M. Green and L. R. Falkner, J. Am. Chem. Soc. **105**, 2950 (1983).