

Electrochromism of Nickel Oxide Thin Film with Polymer Gel Electrolyte

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ABSTRACT: Polymer gel electrolytes were investigated for an electrochromic device (ECD) using nickel oxide thin film. Poly(ethylene oxide) (PEO) derivatives were cross-linked and swelled in KOH-aqueous solution giving a hydrogel electrolyte. The ECD containing the uniformly cross-linked hydrogel showed good result in electrochromic switching performance. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1305–1308, 2002

Key words: electrochemistry; hydrogels; polyethers; crosslinking

INTRODUCTION

Considerable attention has been focused on electrochromic devices (ECD) for their application to a variety of electro-optical devices, such as switchable window, electromagnetic shutter, and light modulation device.^{1–3} We have been studying electrochromic (EC) behaviors of nickel oxide (NiO_x) thin films prepared from an aqueous solution of nickel ammine complex.^{4–6} This method has various merits for the large area devices, including mild formation condition, low stress for atmosphere, and low cost compared with dry processes. Moreover, these NiO_x films exhibited excellent EC characteristics in terms of contrast and charge efficiency ($55 \text{ C}^{-1} \text{ cm}^2$) in alkaline electrolyte solutions.⁵ The construction of a completely solid-type system is desirable for the application to reliable and practical electro-optical devices.

We have assembled an ECD based on NiO_x thin film and polymer gel electrolytes.^{7–10} Polymer complexes consisting of poly(ethylene oxide) (PEO) derivatives and alkali metal salts are known to be solvent-free polymer electrolytes that

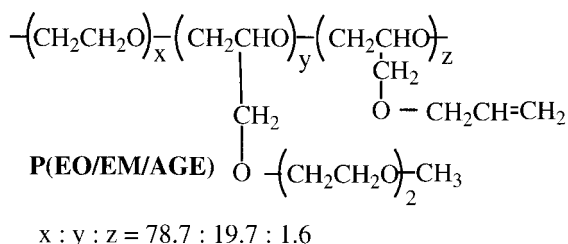
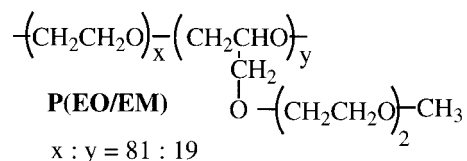
are potentially applicable for use in high-energy-density batteries.^{11–13} The polymer complexes of PEO that can give transparent thin films are expected to contribute to light-modulating devices, although the ion conductivity of the complexes is not as high as that of electrolyte solutions. The electrolyte layer for the ECD based on NiO_x should be proton conductive because proton is indispensable for the EC reaction of NiO_x .^{4–6} The polymer gel electrolyte layer that is thin, uniform, and adhesive to NiO_x thin film will be preferable for the high reproducibility of the ECD. Unique electrolytes containing hydrogel of PEO have been prepared for the ECD.

EXPERIMENTAL

Poly[ethylene oxide-*co*-2-(2-methoxyethoxy)ethyl glycidyl ether] P(EO/EM), poly[ethyleneoxide-*co*-2-(2-methoxyethoxy)ethyl glycidyl ether-*co*-allyl glycidyl ether] P(EO/EM/AGE), and a cross-linking aid were supplied by Daiso Company, Ltd. (Osaka, Japan): P(EO/EM); EO:EM = 81:19; $M_w = 1.1 \times 10^6$, $M_w/M_n = 6.1$ [determined by gel permeation chromatography (GPC) using polystyrene standard samples]; glass transition temperature (T_g) = $-69.5 \text{ }^\circ\text{C}$ [determined by differential scanning calorimetry (DSC)]; P(EO/EM/AGE); EO:

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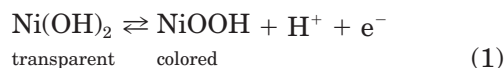


Scheme 1 Structures of P(EO/EM) and P(EO/EM/AGE).

EM:AGE = 78.7:19.7:1.6; $M_w = 1.5 \times 10^6$, $M_w/M_n = 5.8$; $T_g = -69.1$ °C. Poly(vinyl pyrrolidone) (PVP, $M_w = 3.6 \times 10^5$, Tokyo Kasei) was used as received. The structures of P(EO/EM) and P(EO/EM/AGE) are shown in Scheme 1. NiO_x thin films were deposited on ITO (indium tin oxide)-coated (10 × 10 mm) glass plate (25 × 25 mm, 1 mm thickness) by potentiostatic electrolysis (at 1.1 V versus Ag/AgCl) for 8 min of nickel ammine complex solution (pH 9) prepared according to previous works.^{4–6} As an aqueous medium for the hydrogel electrolytes, we adopted a KOH–aqueous solution (pH 10) containing 0.105–0.11 M KOH and 0.05 M K₂B₄O₇ buffer. The polymer gel (polymer solution) electrolyte layer (80 μm thickness) was sandwiched with a ITO-coated glass plate and the NiO_x thin film on ITO, as shown in Scheme 2. Stepping the voltage on the assembled device was given by a potentiostat (Hokuto Denko HA501G) in conjunction with a function generator (HB104), and the absorbance at 400 nm was monitored with an ultraviolet–visible (UV–vis) spectrophotometer (Shimadzu UV-2200).

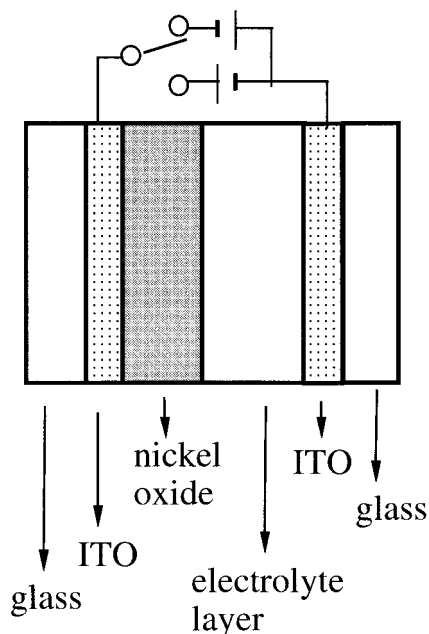
RESULTS AND DISCUSSION

The NiO_x thin film as deposited was dark brown and had absorption band at 400–800 nm. The oxidation of the film contacted with the aqueous solution of electrolyte colored the film more and the reduction de-colored the film as we reported (eq.1):^{4–6}



This equation indicates indispensability of proton for this EC reaction. Almost simple P(EO/EM) containing LiBF₄ and a trace amount of water was used for the electrolyte layer of the ECD based on NiO_x, however, the color did not change for the potential stepping. In the ECD containing the electrolyte layer of KOH–aqueous solution of P(EO/EM) (17 wt %), the chronoabsorptometry for the stepping the voltage between 2 (100 s) and –1.5 V (100 s) exhibited EC behavior as shown in Figure 1. The change of absorbance (ΔA) at 400 nm increased during 10 double potential stepping and then started to decrease. At the 25th double potential stepping, ΔA was <0.09. The absorbance of the reduced state (the minimum of the absorbance) increased according to potential stepings. NiO_x thin film would be bleached incompletely by the reduction. The chronoabsorptometry of similar ECD based on poly(vinyl pyrrolidone) (PVP), which is a typical water-soluble polymer, was not reproducible either during 10 double potential stepping (Fig. 2).

P(EO/EM/AGE) is cross-linkable. The KOH–aqueous solution of P(EO/EM/AGE) (13 wt %) containing potassium persulfate (10 wt % versus the polymer) as a cross-linking agent was placed in the electric oven at 80 °C for 40 min giving



Scheme 2 Schematic illustration of electrochromic device (ECD) featuring polymer gel electrolyte.

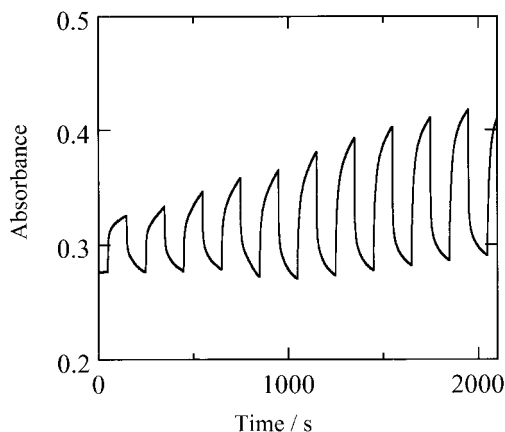


Figure 1 Chronoabsorptometry of ECD containing KOH-aqueous solution of P(EO/EM) for the stepping the voltage between 2 V (for 100 s) and -1.5 V (100 s) monitored by the absorbance at 400 nm.

insoluble gel. The gel looked not to be uniform, involving outer fluid and inner viscous parts. The solution ($8 \mu\text{L}$) of P(EO/EM/AGE) containing potassium persulfate was put on an ITO glass plate and then was placed in the electric oven at 80°C for 40 min under humid conditions, giving transparent gel. The chronoabsorptometry for the ECD with the gel was not reproducible during 10 double potential stepping, as shown in Figure 3.

The acetonitrile solution of P(EO/EM/AGE) (10 wt %), containing azoisobutyronitrile (AIBN, 5 wt % versus the polymer) as a cross-linking agent, was put on an ITO-coated glass plate and was dried for 0.5 h under atmospheric condition to remove the solvent, and then for 24 h under vac-

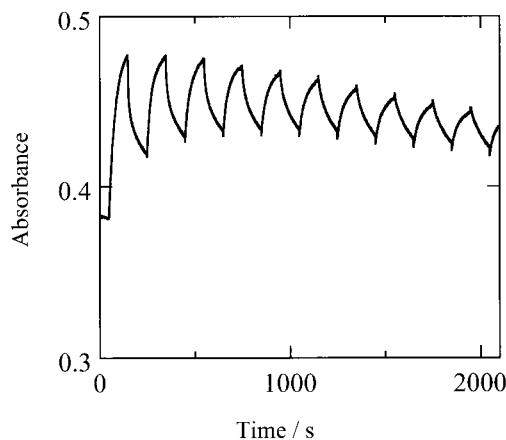


Figure 3 Chronoabsorptometry of ECD containing KOH-aqueous solution of P(EO/EM/AGE) cross-linked under air for stepping the voltage between 2 V (100 s) and -1.5 V (100 s) monitored by the absorbance at 400 nm.

uum at 80°C to give the film. Keeping the film at 80°C under vacuum was expected to cross-link the polymer; however, the film was soluble in water. The solution ($8 \mu\text{L}$) of P(EO/EM/AGE) containing AIBN and a cross-linking aid (1.5 wt % versus the polymer) was put on ITO glass plate and dried under atmospheric condition and then under vacuum at 80°C in a similar way. The film was insoluble in water, indicating the cross-linking aid was effective. The cross-linked film soaked in the KOH-aqueous solution for 18 h was swelled, giving transparent hydrogel. The chronoabsorptometry result of the ECD containing the hydrogel is shown in Figure 4. The ΔA was larger

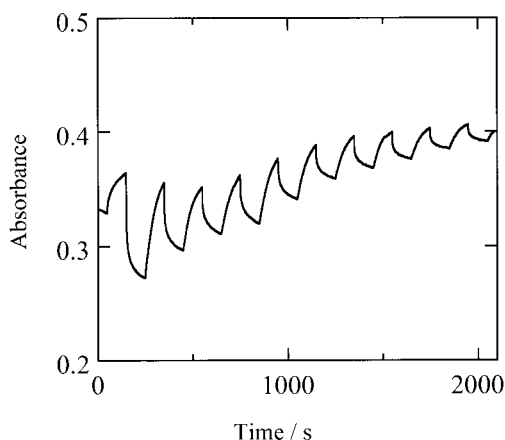


Figure 2 Chronoabsorptometry of ECD containing KOH-aqueous solution of PVP for the stepping the voltage between 2 V (100 s) and -1.5 V (100 s) monitored by the absorbance at 400 nm.

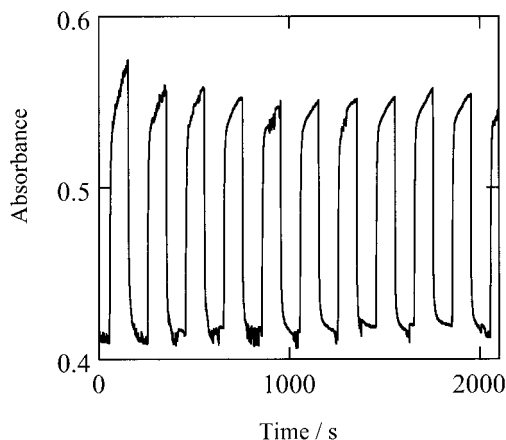


Figure 4 Chronoabsorptometry of ECD containing swelled film of cross-linked P(EO/EM/AGE) for the stepping the voltage between 2 V (100 s) and -1.5 V (100 s) monitored by the absorbance at 400 nm.

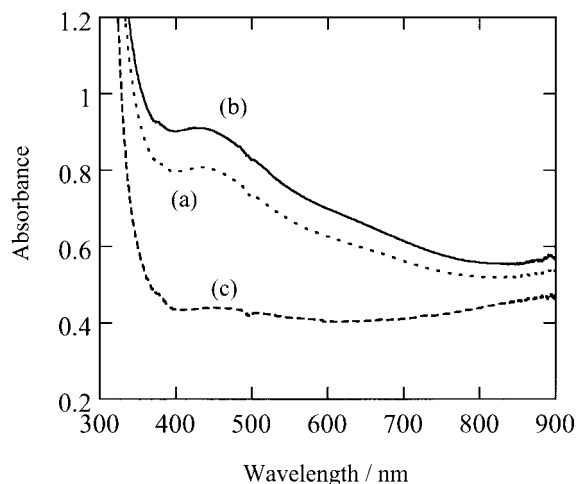


Figure 5 Absorption spectra of ECD containing swelled film of cross-linked P(EO/EM/AGE): (a) as prepared; (b) oxidized at 2 V; (c) reduced at -1.5 V.

than those of the other polymer electrolytes and was reproducible during 20 double potential stepping. The change of visible light absorption of this ECD system, shown in Figure 5, indicated that the EC was identical to that of NiO_x thin film in aqueous solution following eq. 1.⁴⁻⁶

In the case of P(EO/EM) solution (Fig. 1), the concentration of polymer (17 wt %) was larger than that of the hydrogels, and the contact between NiO_x film and the electrolyte would be looser for its lower fluidity.¹⁴ Remarkably, earlier EC deterioration of the device using PVP solution electrolyte (Fig. 2) seems to be due to instability of the polymer in the redox stepping. PVP would possibly be oxidized in the presence of molecular dioxygen and alkaline solution. This will lead to advantage of PEO derivatives.

P(EO/EM/AGE) solution that is cross-linked under air will not be uniform. At the surface of the solution, molecular dioxygen will react with the radical generated from the cross-linking agent to inhibit the cross-linking. Inside the solution, cross-linking will occur because of the lower concentration of molecular dioxygen. Heterogeneous polymer electrolyte is not supposed to be preferable for the reproducibility in the redox stepping, as shown in Figure 3. In contrast the hydrogel suitably prepared by swelling P(EO/EM/AGE) film showed good reproducibility in the redox stepping (Fig. 4). The film would be crosslinked uniformly under vacuum. The cross-linking aid was indispensable for preparing the hydrogel. The mobility of the polymer chain in the film will be smaller than that in the polymer

solution, therefore, the film without the cross-linking aid will not be cross-linked or be cross-linked in low density to be soluble in water. Supposedly this hydrogel is characterized by the comparably high proton conductivity as well as the enough flexibility to assemble the ECD.

The present work has demonstrated that the polymer gel cross-linked uniformly can be used for the electrolyte of ECD. Reliable and practical ECD without liquid electrolyte will be obtained by optimizing the conditions, although the reproducibility and response of the ECD with the hydrogel were, at the present, not as high as those with liquid electrolyte and could not be sufficient for its application to electro-optical device.

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REFERENCES

1. Platt, J.R. *J Chem Phys* 1961, 34, 862.
2. Lampert, C.M. *Solar Energy Mater* 1984, 11, 1.
3. Monk, P.M.S.; Mortimer, R.J.; Rosseinsky, D.R. *Electrochromism: Fundamental and Applications*; VCH: Weinheim, 1995.
4. Chigane, M.; Ishikawa, M. *J Chem Soc Faraday Trans* 1992, 88, 2203.
5. Chigane, M.; Ishikawa, M. *J Electrochem Soc* 1994, 141, 3439.
6. Chigane, M.; Ishikawa, M.; Inoue, H. *Sol Energy Mater Sol Cells* 2000, 64, 65.
7. Passerini, S.; Scrosati, B.; Hermann, V.; Holmblad, C.; Bartlett, T. *J Electrochem Soc* 1994, 141, 1025.
8. Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. *Chem Mater* 1998, 10, 2101.
9. Meeker, D. L.; Mudigonda, D. S. K.; Osborn, J. M.; Loveday, D. C.; Ferraris, J. P. *Macromolecules* 1998, 31, 2943.
10. Taunier, S.; Guery, C.; Terascon, J. M. *Electrochim Acta* 1999, 44, 3219.
11. Bonino, F.; Scrosati, B.; Selvaggi, A.; Evans, J.; Vincent, C. A. *J Power Sources* 1986, 18, 75.
12. Watanabe, M.; Itoh, M.; Sanui, K.; Ogata, N. *Macromolecules* 1987, 20, 569.
13. De Paoli, M.A.; Casalbore-Miceli, G.; Giroto, E. M.; Gazotti, W.A. *Electrochim Acta* 1999, 44, 2983.
14. After soaking cross-linked P(EO/EM/AGE) film in KOH-aqueous solution for 24 h, the film contained 10 times-weight of solution giving hydrogel. The concentration of the polymer in the hydrogel is estimated to be <10 wt %. In contrast 10 wt % P(EO/EM) solution was too fluid to assemble the ECD.