

ELECTROCHEMICAL SYNTHESIS OF ELECTROCHROMIC PRASEODYMIUM OXIDE FILMS IN DMSO₂ MELTS

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The praseodymium oxide and lithium doped- praseodymium oxide films were synthesized onto the ITO electrode by electrolysis in molten dimethylsulphone (DMSO₂)-PrCl₃, DMSO₂-PrCl₃-LiNO₃, and DMSO₂-Pr₆O₁₁-LiNO₃ system at the temperature about 150 °C. The obtained films were characterized by X-ray diffraction, spectroscopic measurements and electrochemical measurement. Moreover, the electrochromic (EC) reactions of the oxide films in solution of propylene carbonate (PC) were investigated. The absorption spectrum of praseodymium oxide (Pr_xO_y) films obtained by electrodeposition in DMSO₂-PrCl₃ systems had 560nm and 390nm peaks due to mixed valence of Pr²⁺ and Pr³⁺ and in DMSO₂-Pr₆O₁₁-LiNO₃ systems had 640nm and 410nm peaks due to mixed valence of Pr³⁺ and Pr⁴⁺. The color changes of EC reactions of the deposited Pr_xO_y films became more clearly by annealing the deposited films.

1. INTRODUCTION

Recently, the electrolytic deposition method has been actively investigated as a powerful technique for the large area chromogenic thin film. The synthesis experiments have been done in aqueous solution [1]. It is difficult to get lithium vanadium bronze films with high lithium content and less water by electrolysis in aqueous solution. So we have a try to synthesize lithium vanadium bronze films from non aqueous solution, the molten salt of low temperature (<250 °C). The lithium vanadium bronze films can be formed directly by electrolysis without evaporation, and its glue onto ITO glass can be improved, too. Since the films is synthesized from high temperature solution, it might be used at comparatively high temperature EC device (> 100 °C). The EC praseodymium oxide films formed by MOCVD method using molecular organic gases was reported [2].

By the way, DMSO₂ which is a kind of inert solvent with melting point about 108 °C, has been studied as the electrolyte of secondary lithium battery [3].

We used DMSO₂-V₂O₅ and DMSO₂-V₂O₅-LiNO₃ systems in the previous paper [4].

Due to the effect of LiNO₃, DMSO₂-V₂O₅-LiNO₃ system has higher basicity than DMSO₂-V₂O₅ system; the lithium vanadium bronze was successfully synthesized from DMSO₂-V₂O₅-LiNO₃ (1mol%) system. In this report, the EC properties of the deposited praseodymium oxide films on ITO formed in electrolytic bath of DMSO₂-PrCl₃ system and DMSO₂-Pr₆O₁₁ system by electrolysis. And, the addition effects of LiNO₃ to DMSO₂ melt containing PrCl₃ or Pr₆O₁₁ were investigated.

2 EXPERIMENTAL

2.1 Synthesis of praseodymium oxide and lithium doped praseodymium oxide films

Praseodymium chloride PrCl₃ (99.99%), praseodymium oxide Pr₆O₁₁ (99.99%) and DMSO₂ in these experiments were commercial reagent grade. The praseodymium oxide and lithium doped praseodymium oxide films were

synthesized onto the ITO electrode by electrolysis in molten DMSO₂-PrCl₃/Pr₆O₁₁, DMSO₂-PrCl₃/Pr₆O₁₁-LiNO₃, DMSO₂-PrCl₃-Pr₆O₁₁ and DMSO₂-PrCl₃-Pr₆O₁₁-LiNO₃ at 150 °C. The praseodymium content in electrolytic solution was determined by ICP analysis. Using the ITO (Indium Tin Oxide, 10 Ω per square cm, surface area 3.5 cm²) glass as a cathode, the platinum wire (diameter 0.5 mm) was used for the anode and reference. Prior to electrolysis, cyclic voltammograms were recorded in order to determine the redox potential of praseodymium ions in the melt using a potentiogalvanostat. The electrolysis was carried out with a constant voltage (-1.0 V ~ -1.5 V) in air, the current changed within 0.0 mA ~ 1.0 mA and the quantity of electricity was about 50 mC ~ 1000 mC. The vanadium bronze film was deposited onto the ITO electrode by controlling the electrolytic condition. The obtained films were dried in air or annealed at 400 °C for 4 hours after drying in air.

2.2 Characterization of praseodymium oxide films

The obtained films were analyzed by x-ray diffraction (XRD) Moreover, the relationship between coloration and the changes of potential was investigated by measuring cyclic voltammogram in the 0.5 mol dm⁻³ LiClO₄/PC solution with the reference electrode of Ag/Ag⁺ at room temperature. The optical absorption spectra of the films as-deposited were measured on spectrophotometer at the wavelength range of 300 ~ 900 nm in air at room temperature with ITO reference.

3. RESULTS AND DISCUSSION

3.1 The electrolytic condition, composition and solubility of solute.

The praseodymium ions contents dissolved in electrolytic melts of (DMSO₂)-PrCl₃/Pr₆O₁₁, and DMSO₂-PrCl₃/Pr₆O₁₁-LiNO₃ system at 150 °C. The highest solubility of praseodymium was found in DMSO₂-PrCl₃

Pr₆O₁₁ system. (Pr: 9.23 mg /1g DMSO₂). Table 1 shows the solubility of praseodymium oxides and chlorides in the electrolytic bath of DMSO₂ melts and DMSO₂ melt dissolving LiNO₃ (1mol%) at 150°C.

Table 1. Solubility of praseodymium chlorides and oxides in electrolytic DMSO₂ melts at 150°C

Electrolytic composition	Pr mg/1gDMSO ₂
DMSO ₂ - PCl ₃	1.65
DMSO ₂ - PrCl ₃ - LiNO ₃	0.197
DMSO ₂ - Pr ₆ O ₁₁	0.124
DMSO ₂ - PrCl ₃ -Pr ₆ O ₁₁	9.23
DMSO ₂ - PrCl ₃ -Pr ₆ O ₁₁ -LiNO ₃	7.26

The electrolysis of DMSO₂-PrCl₃ system at 150 °C was carried out in the following conditions: (1) electrolytic potential of -0.5 V, (2) electrolytic potential of -1.0 V, (3) electrolytic potential of -1.5 V, (4) electrolytic potential of -2.0 V, quantity of electricity: 200 m C, 500 m C and 1000 m C. Under condition (1), the film could not be obtained. But under condition (2) and (3), a slightly blue transparent thin film was obtained. Under condition (4), the ITO glass electrode colored to black and lost electronic conductivity. It was observed that the thickness of film was not uniform when the quantity of electricity became more than 200 mC. From the above experiments, it was found that the potential is within the range of -1.0 V~-1.5 V and the quantity of electricity for electrode deposition was less than 200 mC as a suitable electrolytic condition.

But, the electrolysis of DMSO₂- Pr₆O₁₁ and DMSO₂-Pr₆O₁₁-LiNO₃ system carried out at -1.4V, 100mC, the cathode ITO films had very slightly blue color. In these systems, it is difficult to obtain the thin oxide films. In DMSO₂-PrCl₃-Pr₆O₁₁ and DMSO₂-PrCl₃-Pr₆O₁₁-LiNO₃ system at 150°C the thicker films were obtained easily.

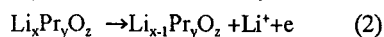
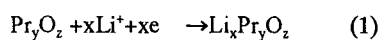
3.2 The XRD pattern of the deposited oxide on ITO

The XRD pattern shown in Fig.1 indicates the formation of praseodymium oxides (Pr_xO_y) from DMSO₂-PCl₃ systems and DMSO₂-PrCl₃-LiNO₃ system.

The film was calcined at 400°C for 4 hours in order to evaporate DMSO₂ involved in deposited oxide. The XRD pattern was not changed by annealing. The formation of lithium doped praseodymium oxides (Li_xPr_yO_z) were assumed formed the XRD pattern of the deposited oxide formed from DMSO₂-PrCl₃-Pr₆O₁₁-LiNO₃. The XRD and ICP were used for the qualitative analysis of Pr_xO_y and Li_xPr_yO_z.

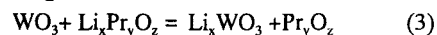
3.3 The electrochromic character of the deposited oxide on ITO

In this work, the electrochromic properties can be described as a reaction:



A practical electrochromic device whose electrode is made of WO₃ and Li_xV₂O₅ is based on a kind of very reversible electrochromic reaction named rocking

chair reaction. And the similar reaction with Li_xPr_yO_z may be thought as follows:



The cyclic stability and Li intercalation rate are two important factors for electrochromic reaction in practical electrochromic device.

The cyclic voltammograms of praseodymium oxide (Pr_xO_y) films obtained by electrodeposition in DMSO₂-PrCl₃ systems at -1.0V with 100 mC, were shown in Fig.2. And the absorption spectrum of these praseodymium oxide films had 560 nm and 390 nm peaks. These peaks are different to 3 valent praseodymium ions in aqueous solution shown in Fig. 3(d). It may be attributed to mixed valence of Pr³⁺ and Pr²⁺. And the effect of lithium ion intercalation or deintercalation is shown in the Fig.3.

The annealing effect for the deposited films is shown in the Fig.2 (2). The conductivity of the films was improved by annealing. Also, the annealing effects were observed with considering the spectrum changes from Fig.3 (a) to Fig.4 (a). These peaks at 560nm and 390nm shifted to 550nm and 360nm. This blue shift of absorption peaks and the narrowing of band width by annealing were useful to EC reaction. And the color change of EC reaction became more clear by annealing of the deposited films. The addition effects of LiNO₃ and Pr₆O₁₁ to electrolytic bath of DMSO₂-PCl₃ system were shown in Fig.5, 6 and 7. The increase of basicity of electrolytic bath and the formation of lithium doped vanadium bronzes (Li_xV₂O₅) by addition of LiNO₃ to the electrolytic bath of DMSO₂ melt, were reported by our previous paper [4].

The similar addition effects of LiNO₃ to the electrolytic bath of DMSO₂-PrCl₃ system DMSO₂-Pr₆O₁₁ system were expected. The conductivity of the electrolytic bath and the deposited Li_xPr_yO_z ITO electrode was increased, and the red shifts of the peaks of absorption spectrum were observed. These changes by addition effects of LiNO₃ were shown in Figs.5 and 6. And the absorption spectrum of the deposited films formed in DMSO₂-Pr₆O₁₁-LiNO₃ systems was shown in Fig.7. This spectrum has 640nm and 410nm peaks and considerably different from the spectrum of the deposited films formed in DMSO₂-PrCl₃-LiNO₃ system. It may be attributed to mixed valence of Pr³⁺ and Pr⁴⁺.

Therefore, It may be assumed that the EC properties of the deposited Pr_xO_y films on ITO have the charge transfer type color due to the mixed valence, such as WO₃ films.

4. CONCLUSION

The praseodymium oxide films were obtained by electrolysis with -1.0 V~-1.5 V and less than 200 mC in DMSO₂ melts at 150°C. The absorption spectrum of praseodymium oxide films obtained by electrodeposition in DMSO₂-PrCl₃ systems had 560nm and 390nm peaks due to mixed valence of Pr³⁺ and Pr²⁺. And the absorption spectrum of lithium doped praseodymium films obtained in DMSO₂-Pr₆O₁₁-LiNO₃ systems had 640nm and 410nm peaks due to mixed valence of Pr³⁺ and Pr⁴⁺. The EC reaction of the deposited praseodymium oxide films formed by electrochemical reaction in DMSO₂ melt dissolving praseodymium chloride and oxides, was recognized as the charge transfer type color due to the mixed valence, such as WO₃. The color change of EC

reaction became clearer by annealing of the deposited films.

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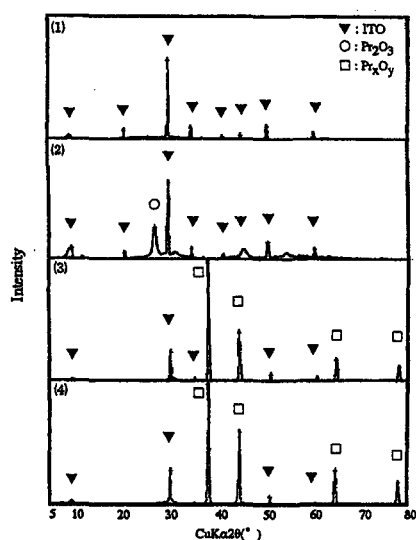


Fig.1 The XRD pattern of deposited films on ITO formed in $\text{DMSO}_2\text{-PCl}_3$ system

- (1) ITO
- (2) Pr_2O_3 -ITO (vacuum evaporated films)
- (3) As deposited films on ITO formed in $\text{DMSO}_2\text{-PCl}_3$ system
- (4) The deposited films on ITO annealed at 400°C for 4 hrs

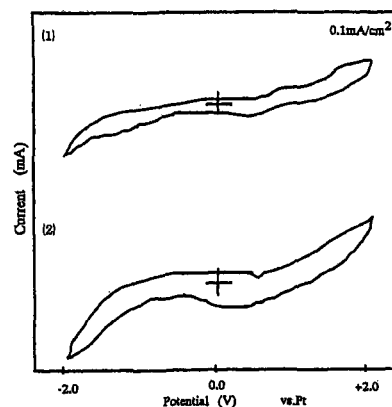


Fig.2 Cyclic voltammograms of the deposited Pr_xO_y films on ITO formed in electrolytic bath of $\text{PDMSO}_2\text{-PCl}_3$ system
(1) The as deposited Pr_xO_y ITO electrode
(2) The Pr_xO_y ITO electrode annealed at 400°C for 4 hrs

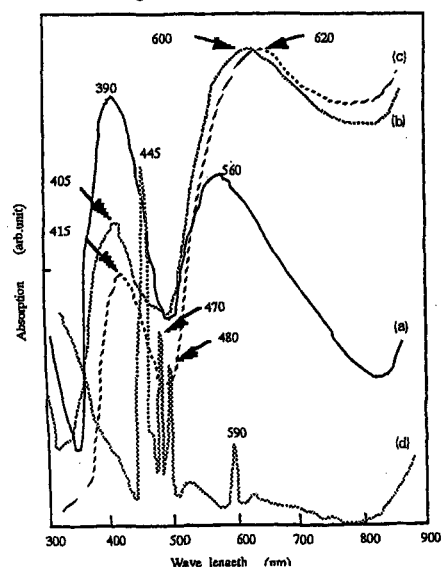


Fig.3 Potential dependence of absorption spectra of Pr_xO_y films on ITO formed in electrolytic bath of $\text{PDMSO}_2\text{-PCl}_3$ system
(a) The as deposited Pr_xO_y films on ITO formed at -1.0V , 100mC
(b) 1.0V , 50mC in PC solution
(c) -1.0V , 50mC in PC solution
(d) Pr^{3+} standard solution (100ppm)

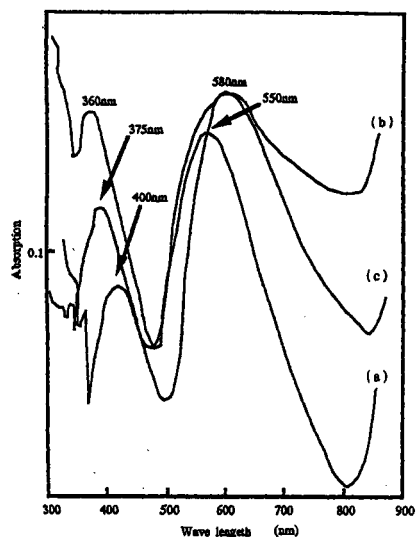


Fig.4 Potential dependence of absorption spectra of the annealed praseodymium oxide films on ITO in PC solution

- (a) Annealed Pr_2O_3 films on ITO
(b) At 1.0V in PC solution
(c) At -1.0V in PC solution

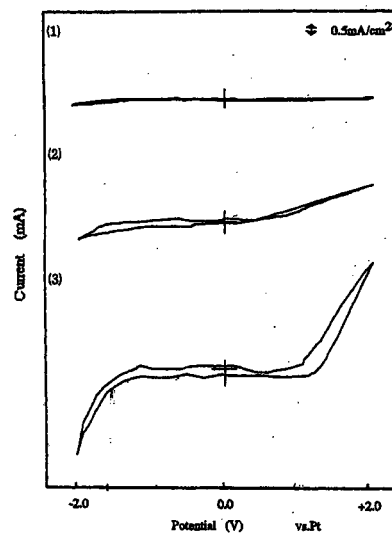


Fig.5 Cyclic voltammograms of electrolytic bath of (1) DMSO_2 , (2) $\text{DMSO}_2\text{-PCl}_3$ and (3) $\text{DMSO}_2\text{-PCl}_3\text{-LiNO}_3$ system with ITO electrode

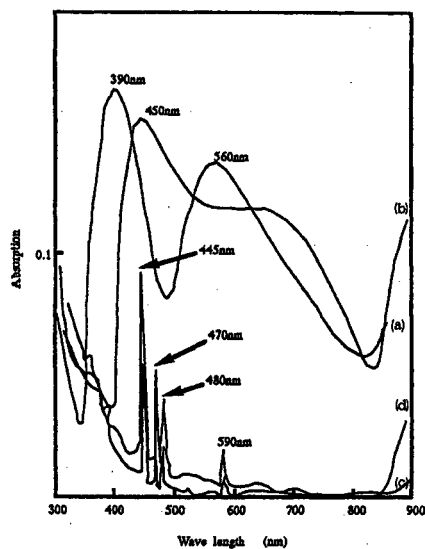


Fig.6 Absorption spectra of the deposited films on ITO formed in (a) $\text{DMSO}_2\text{-PrCl}_3$, (b) $\text{DMSO}_2\text{-PrCl}_3\text{-LiNO}_3$ system, (c) Electrolytic bath of $\text{DMSO}_2\text{-PrCl}_3\text{-LiNO}_3$ system and (d) Pr^{3+} standard solution (100ppm)

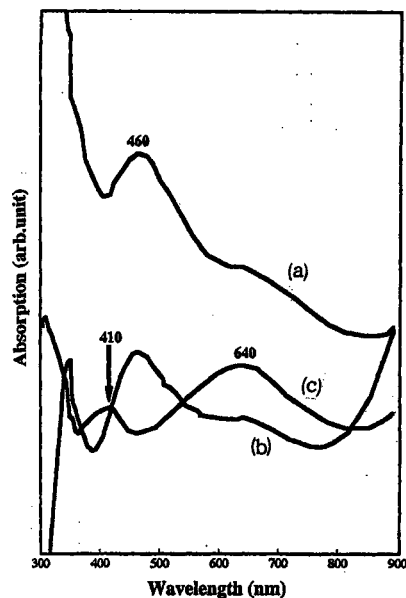


Fig.7 Absorption spectra of the deposited films on ITO formed in (a) $\text{DMSO}_2\text{-PCl}_3$, (b) $\text{DMSO}_2\text{-PCl}_3\text{-LiNO}_3$ system, (c) $\text{DMSO}_2\text{-Pr}_6\text{O}_{11}\text{-LiNO}_3$ system

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