

Characterization of electrodeposited Ce-Co mixed oxide thin films for transparent counter electrode for electrochromic device

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Thin films consisting of Ce and Co oxides were prepared by cathodic electrodeposition from mixtures of $\text{Ce}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_2$ aqueous solutions with molar mixture ratios of Ce/Co=0.1,0.5,1 and 10. X-Ray diffraction(XRD) shows that all the composite films are amorphous while single oxides of Ce and hydroxide of Co are crystalline. In IR spectra, only the film deposited from a solution of Ce/Co=1 has a new peak at 767cm^{-1} that can be attributed to the formation of Ce-O-Co band. More important, this film only leads to an increase in the overall charge capacity in cyclic voltammetry and also is highly transparent with a transmittance about 0.85 for oxidation and reduction state in UV-vis spectra. This indicates that the composite oxide thin film cathodically electrodeposited from the solution with a mixture ratio Ce/Co=1 has desirable characteristic for a counter electrode for electrochromic devices.

Keywords: Electrochromic device, Transparent Counter Electrode, Electrodeposition

1. INTRODUCTION

Thin films of mixed CeO_2 and transition metal oxides have recently attracted interest because of their desirable properties for being counter electrodes in electrochromic devices.¹⁻⁵⁾ We attempted to prepare such mixed oxide thin films electrode by electrodeposition. Dry processes such as sputtering and evaporation or the sol-gel method as a wet process have been used to prepare electrochromic films. The sol-gel method is especially suited for fabrication of films on large-area substrates because of its high forming rate and uniformity in film deposition. However control of film formation in this process is not easy, and subsequent heat treatment is indispensable in order to convert the metal salt to metallic form and to crystallize the matrix oxide. Electrodeposition which is also a wet process, has advantages of good controllability of deposition based on the

charge passed during electrolysis. We have been studied about Co oxide films⁶⁾ and Ir-Co mixed oxide films⁷⁾ prepared by electrodeposition previously.

In this paper, we report on the preparation of composite thin films consisting of Ce and Co oxides by electrodeposition and describe their morphology, crystal structure and electrochromic properties.

2. EXPERIMENTAL

Ce-Co mixed oxide films were cathodically electrodeposited on ITO glass substrates from 0.01M~0.001M solutions of $\text{Ce}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_2$ mixed electrolyte with different ratios at a current density of $500 \mu\text{A}/\text{cm}^2$ for 5min. at room temperature. The films were characterized by IR and XRD, and observed by SEM. Cyclic voltammograms of the films in 0.05 mol dm^{-3} NaOH aqueous solution were measured using a potentiostat with a function generator (HOKUTO HB 301,HB

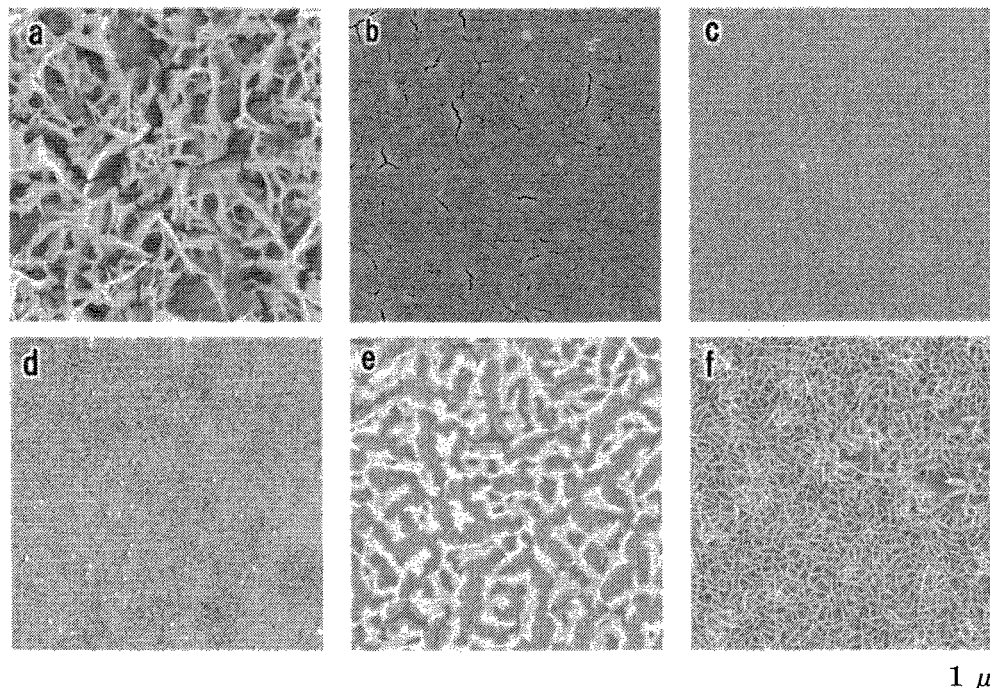


Fig.1 SEM images of the surface of the CeO_2 , Ce/Co mixed oxide and Co(OH)_2 films deposited on ITO glass electrode

a) CeO_2 b) $x = 10$ c) $x = 1.0$ d) $x = 0.5$ e) $x = 0.1$ f) Co(OH)_2
($x = \text{Ce/Co}$)

105). A glassy carbon and Ag/AgCl electrodes were used as counter and reference electrodes respectively.

3. RESULT AND DISCUSSION

3-1 Morphologies of the films

In Figure 1 (a-f), different surface morphologies of the cathodically deposited films from (a) $0.01 \text{ mol dm}^{-3} \text{ Ce(NO}_3)_3$ solution, (b) $0.01 \text{ mol dm}^{-3} + 0.001 \text{ mol dm}^{-3} \text{ Co(NO}_3)_2$, (c) $0.01 \text{ mol dm}^{-3} \text{ Ce(NO}_3)_3 + 0.01 \text{ mol dm}^{-3} \text{ Co(NO}_3)_3$, (d) $0.005 \text{ mol dm}^{-3} \text{ Ce(NO}_3)_3 + 0.01 \text{ mol dm}^{-3} \text{ Co(NO}_3)_3$, (e) $0.001 \text{ mol dm}^{-3} \text{ Ce(NO}_3)_3 + 0.01 \text{ mol dm}^{-3} \text{ Co(NO}_3)_3$, (f) $0.01 \text{ mol dm}^{-3} \text{ Co(NO}_3)_2$. The surfaces are (a) uneven and of withered twig structure, (b) smooth but has some cracks, (c) very smooth and homogeneous (d) smooth but contains two kinds of particles, (e) a striped pattern structure, (f) porous and of petals structure and porous. The surfaces of the composite oxide films are much smoother and more homogeneous than the surfaces of single oxide and hydroxide films. The optimum

Ce/Co ratio to obtain the most smooth and homogeneous surface is 1.0

3-2 XRD analysis

The XRD patterns revealed that the electrodeposited oxides from single salt baths were crystalline. CeO_2 from $0.01 \text{ mol dm}^{-3} \text{ Ce(NO}_3)_3$ solution contains four patterns CeO_2 (111), (200), (220), (311) of cubic cerianite, while the XRD pattern of Co(OH)_2 from $0.01 \text{ mol dm}^{-3} \text{ Co(NO}_3)_2$ solution consisted of mixed crystallites of α - Co(OH)_2 and β - Co(OH)_2 . However, all composite oxides are of amorphous structure.

3-3 IR spectra of films

The IR absorption spectra of cathodically deposited of Ce-Co film (Ce/Co=1) heated at 400°C for 1h (a), Ce-Co film (Ce/Co=1) as deposited (b), CeO_2 (c), and Co(OH)_2 (d) are shown in Fig.3. The high peak at 3490 cm^{-1} for (a), (b), (c), (d) films are attributed to O-H stretching vibration. Furthermore, another peak at 1390 cm^{-1} for (b), (c), (d) indicate of

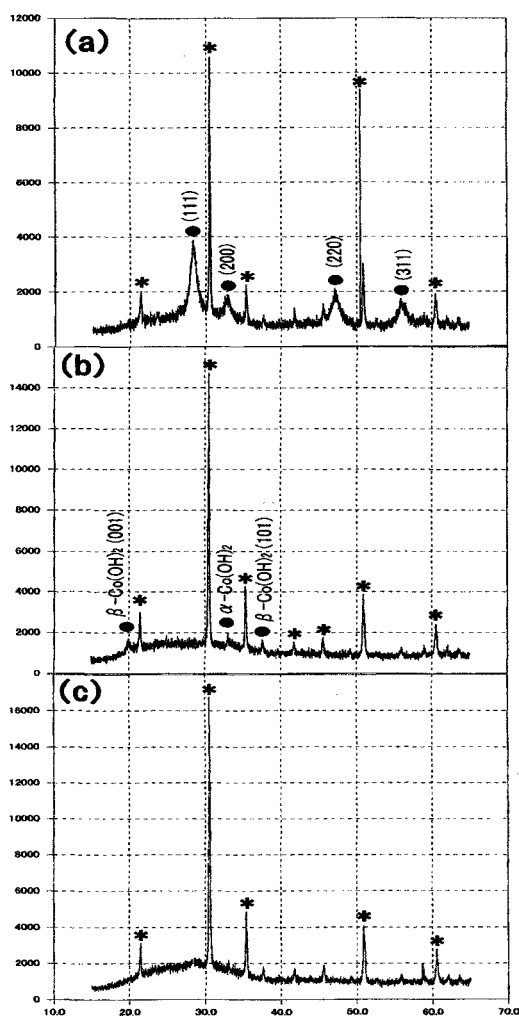


Fig.2 XRD Patterns (a) CeO_2 film (b) $\alpha + \beta$ Co(OH)_2 film and (c) Ce-Co mixed film. * denotes the diffraction peaks of ITO glass substrates

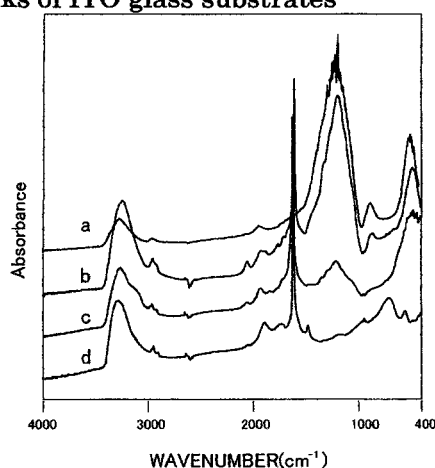


Fig. 3 Infrared absorption Spectra (a) Ce-Co mixed oxide film ($\text{Ce/Co} = 1$) after heating at 400°C (b) Ce-Co mixed oxide film ($\text{Ce/Co} = 1$) as deposited (c) CeO_2 electrodeposited film (d) Co(OH)_2 electrodeposited film

remaining NO_3^- which from nitrate

electrolyte. Also, the peaks at 1050 cm^{-1} in the spectra for (a),(b),(c) are attributed to Ce-O terminal stretching. New band at 767 cm^{-1} for (a),(b) indicates formation of Ce-O-Co band. The peak of at 468 cm^{-1} is attributed to Ce-O-Ce deformation.

3-4 Electrochromic properties

First we examined the cyclic voltammograms (C.V) of two single oxide films of CeO_2 and Co(OH)_2 . Cathodically deposited white films of CeO_2 provided a broad peak in negative potential region at $-900\sim 0\text{ mV}$. Cathodically deposited Co(OH)_2 films as grown were of emerald color. The observed electrochromic color change of the films was from brown at oxidation state to pale brown at reduction state. The C.V curve showed redox peaks in the positive potential region of $0\sim 600\text{ mV}$.

Ce/Co oxide film ($x=10$) showed pale white color. Its' cyclic voltammogram curve was similar to that of CeO_2 film. Ce/Co films ($x=0.1$) showed yellow green color and C.V curve was similar to that of Co(OH)_2 film. The film of Ce/Co oxide ($x=1$) was almost transparent. The shapes of the C.V curve for a mixed oxide film is a sum of the currents of parent oxide materials that consist of the film in terms of redox peaks in positive and negative potential regions of $-600\sim 600\text{ mV}$. The mixed Ce/Co film ($x=1$) thus we have obtained by electrodeposition could provide necessary characteristics to be used as an electrochromic counter electrode.

UV-visible spectra of the film of Ce and Co oxide (a), CeO_2 (b), Co(OH)_2 (c) presented in fig 5. The spectra of the colored and bleached states were measured after the films were charged / discharged for 100 sec at -1 v and 1 v in 0.05 mol dm^{-3} NaOH solution. It seems that the films of (a) the deposited from Ce/Co =1 mixed solution (b) CeO_2 and (c) Co(OH)_2 showed electrochromic optical change by

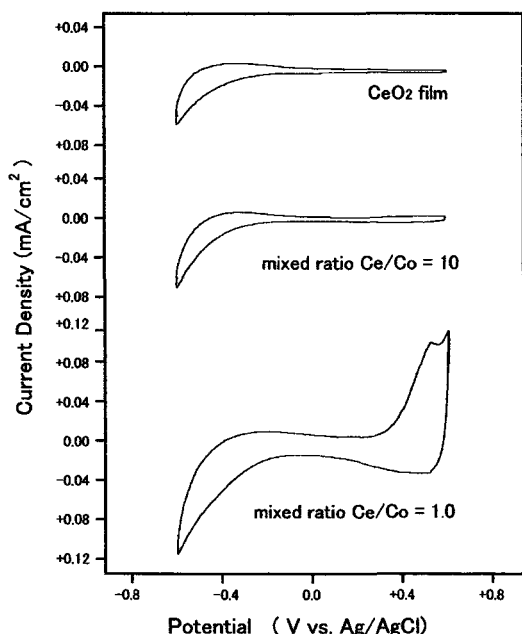


Fig.4 Cyclic voltammogram of CeO₂ film and Ce-Co mixed oxide films

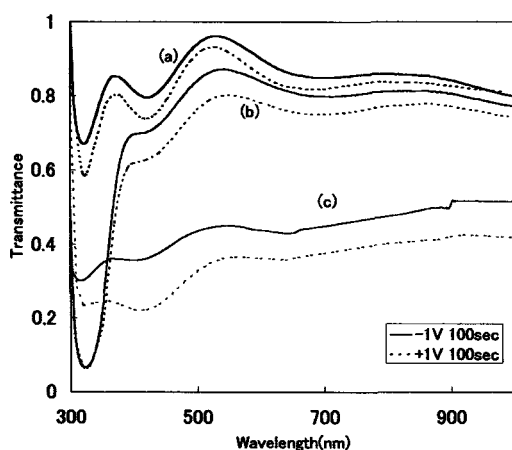


Fig.5 UV-visible spectra of Ce-Co Oxide films (a) Ce/Co = 1 (b) CeO₂ (c) Co(OH)₂

intercalate / deintercalate of OH⁻ ions.

4. CONCLUSIONS

The thin films consisting of Ce and Co oxides are prepared by cathodically electrodeposition.

XRD spectra revealed that the parent material of CeO₂ and Co(OH)₂ were crystalline, but the composite oxides were amorphous. From IR spectra of the composite films revealed a new peak at

767cm⁻¹ that existed neither CeO₂ nor Co(OH)₂. The peak was assigned to Ce-O-Co bridging vibration.

Cyclic voltammetry showed that the composite deposit (Ce/Co = 1) leads to an increase in the overall charge capacity.

The composite oxide film (Ce/Co=1) was fully transparent, giving a transmittance of about 0.85 in uv-visible region.

These results suggest that Ce and Co composite oxide thin film with Ce/Co ratio =1 is a prospect for as optically passive transparent counter-electrode of EC devices.

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