

Some Effects of Co on the Electrochromic Properties of NiO_xH_y Film

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Abstract Some effects of Co addition upon the electrochromic characteristics of a nickel hydroxide film were studied. The films were electrodeposited on both polished Ni plate and conductive ITO glass. The electrochemical behaviors were investigated using the film on Ni plate by linear potential sweep, a. c. impedance, and anodic polarization curves for OER (oxygen evolution reaction). It was found that Co can lower the working voltage and raise the oxygen overpotential, but has little effect on the reaction kinetics. It was also found that the Co can improve the optical properties of the electrochromic film.

Key words Electrochromic, NiO_xH_y film, Co

1 Introduction

The electrochromic materials have a good applied prospect. They are used widely on smart windows with controllable throughput of radiant energy and electronic information displays^[1,2]. In recent years, research on the smart windows has been receiving more and more attention. By controlling the solar radiation to buildings or automobile interiors, one can modify the illumination and heats gain to improve comfort and energy conversion, taking the advantage of low power requirement. Among the electrochromic materials used in smart windows, NiO_xH_y has attracted much attention recently due to its high coloring efficiency, low material cost and high stability, especially its "grey effect"^[3,4]. Besides working as the promising electrochromic material, NiO_xH_y is also a positive material used widely in alkaline secondary batteries, such as Ni/MH battery. Being this kind of material, it usually uses Co as a much efficient additive for improving its properties. A certain content of Co can lower the reaction potential^[5], raise the oxygen evolution potential^[6], increase the conductivity^[7], and prolong its cycle life^[8].

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There are several methods to prepare NiO_xH_y film such as electrodeposition^[2,9], sputter deposition^[1,3], chemical vapour deposition^[10] and electron beam deposition^[11] etc. In this work we prepared the NiO_xH_y film containing low content Co by cathodic co-deposition and studied the effects of it on the electrochromic properties.

2 Experimental Procedures

2.1 Electrode substrates

In this work, the NiO_xH_y thin film samples were cathodically deposited onto both metallic nickel and conductive indium-tin oxide (ITO) coated glass plate. The nickel plate is 99 % pure and 1.5 mm thick, machined to give a surface area of $3 \times 3 \text{ cm}^2$. It was polished with several grades of emery paper, the last being 800. After being cleaned, the plate was electrochemically polished. A nickel wire was spot welded onto the edge of the plate. The sides, the back and the wire were insulated with epoxy resin. The size of the ITO glass plate is $2 \times 2 \times 0.05 \text{ cm}^3$. The ITO coating has a sheet resistance of $80 \sim 100 \ \Omega / \square$. After being sonicated in toluene, acetone and ethanol, each piece of the glass was attached with Ni wire by silver epoxy.

2.2 Film deposition and analysis

The electrolyte used to deposit the NiO_xH_y film was 0.01 mol/L $\text{Ni}(\text{NO}_3)_2$ and a mixture of 0.01 mol/L $\text{Ni}(\text{NO}_3)_2$ containing 10 % $\text{Co}(\text{NO}_3)_2$. The film was deposited at $40 \ \mu\text{A} / \text{cm}^2$ onto Ni plate and $20 \ \mu\text{A} / \text{cm}^2$ onto ITO glass for 8 minutes, using a piece of Ni foam as the counter electrode. The content of Co in the film was determined by dissolving the film in acetic acid and analyzing the solution with WFXID Atomic Absorption Spectro-photometer. The scanning electron micrograph of the films was obtained with a Hitachi X-650.

2.3 Properties Measurements

Electrochemical measurements were carried out with a standard three electrodes system in 1 mol/L KOH solution, using a HgO/Hg reference electrode and a large area Ni foam as the counter electrode. Linear sweep voltammetry (LSV) and anodic polarization experiments were performed using TD3690 potentiostat and the wave form generator controlled by a HP286 computer. The potential range of the LPS is $-0.6 \sim -0.7 \text{ V}$. The anodic polarization was carried out potentiodynamically from 1 to 0.45 V at a scanning rate of 0.5 mV/s. All the potentials mentioned above are referred to a HgO/Hg electrode. a. c. Impedance measurements were performed with a Solartron 1250, associated with the TD3690 potentiostat. The frequency range was 10 kHz to 0.1 MHz and the amplitude is 5 mV. The electrodes were cycled at 10 mV/s several times until the shape of the voltammogram became constant before the electrochemical properties were measured.

Spectral transmittance and reflectance experiments were performed from 300 nm to 2500 nm, using Shimadzu UV365 Spectrophotometer. A electrochemically polished Ni plate was used as the reference mirror when the reflection measurement of the NiO_xH_y film on Ni plate was un-

dertaking.

All of the experiments were carried out at room temperature.

3 Results and Discussion

3.1 Film deposition and structure

The deposition of Ni hydroxide on substrate occurs in response to the rise in pH which accompanies the electrochemical reduction of NO₃⁻ [9]. The films' thicknesses were calculated as 42 nm on Ni plate and 21 nm on ITO glass, assuming the deposition current efficiency is 100% [9,12,13]. The content of Co was determined by analyzing the film on Ni plate and the value is 16.2%. The whole amount of the Ni and Co in acetic acid is 6.34 μg/mL. Under the same condition, a Ni plate was immersed in acetic acid and the dissolved Ni is 0.5 μg/mL, which is less than the 1/10 of the former. Moreover, the hydroxide film always dissolved first. So the dissolution of the Ni substrate is ignored.

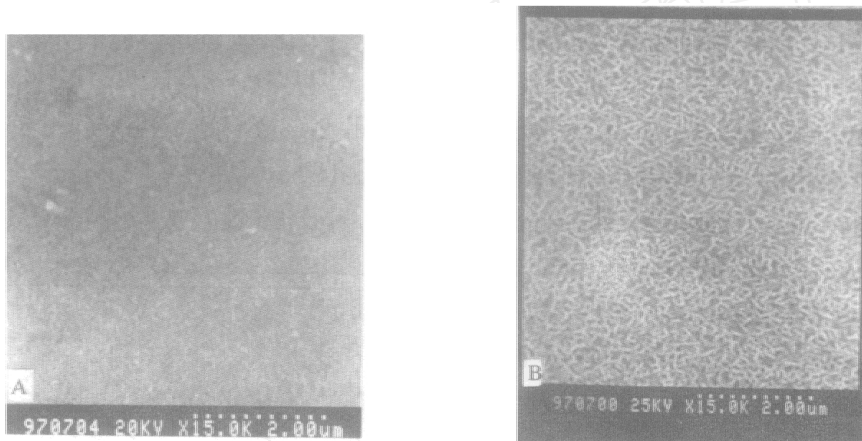


Fig. 1 SEM photographs of the pure (A) and composite (B) NiO_xH_y films on ITO substrate

The surface morphology of the films on ITO glass is shown in Fig. 1. The pure NiO_xH_y exhibited a compact structure, which differs significantly from the structure of the composite one containing Co. The latter has a more porous surface consisting of tangled interconnecting ridges.

3.2 Optical Spectroscopy

The optical properties of the NiO_xH_y films were characterized on both Ni plate and ITO glass. The reflection and transmittance of 300~2500 nm radiation were measured for the film on Ni plate and ITO glass respectively. The electrochromic transformation was carried out in 1 mol/L KOH. The coloration reaction is usually to be written as:



bleached colored

The NiO_xH_y film on Ni plate was B-C (bleached-colored) cycled by linear potential sweep from

0 ~ 600 mV. Then, the electrode was kept at 0 mV for 5 min to be held as the bleached state and at 600 mV for 5 min as the colored one. For the film on the ITO glass, the potential was kept at 700 mV to be the colored state due to the resistivity of their substrate.

Fig. 2 shows the 300 ~ 2 500 nm optical transmittance of the pure NiO_xH_y film and the composite one containing 16.2 % Co at the colored and bleached state on ITO glass. The transmittance of the colored film decreased with the addition of Co. For example, at 550 nm, the data are 63.1 and 57.7 for the pure and composite ones respectively. For such a thin film, the difference was considerable. The reason maybe that the addition of Co increase the utilization of the active material. Meanwhile, there are a little difference between the transmittances of their bleached states and they are very similar to the ITO substrate. Thus, the optical modulation range of transmittance and light wave is widened.

The reflectance character of the two kinds of films on Ni plate between 300 ~ 2 500 nm was shown in Fig. 3. For both the pure and composite films, the reflectance of colored state is lower than the bleached one in the range of 300 ~ 1 200 nm, and when the wave is longer, the former is higher than the latter. The additive of Co has an effect on the property too. When the optical wavelength is in the range of 300 ~ 1 200 nm, the reflectance difference between the colored and bleached state of the composite Ni-O film is smaller than the pure one, while the wave is between 1 200 ~ 2 500 nm, the difference is greater for the composite ones due to the additive of Co. The Co can improve the coloring transformation in the NIR (near infra-red) range. The further study of the problem will probably make the material be used in the field of temperature controlling by exploit solar en-

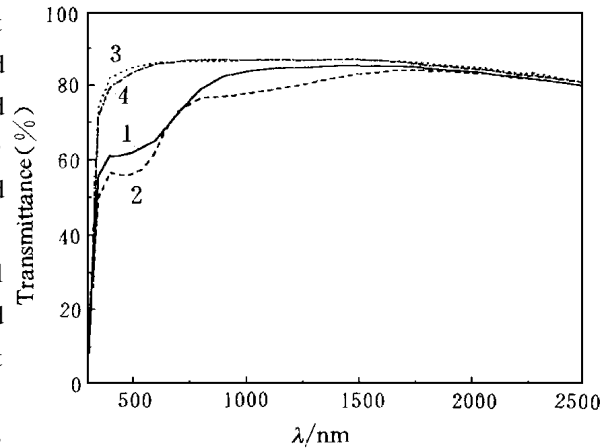


Fig. 2 The optical responses of the pure and composite NiO_xH_y films on ITO substrate

- 1) Colored state of Ni-O film
- 2) Colored state of Ni-O film cont Co
- 3) Bleached state of Ni-O film
- 4) ITO glass

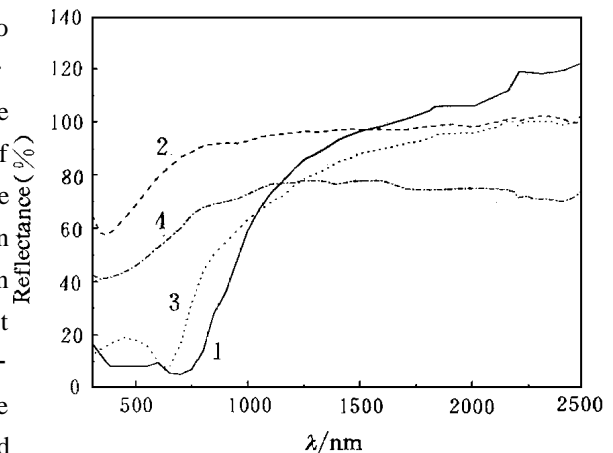


Fig. 3 The optical response of the pure and composite NiO_xH_y films on Ni substrate

- 1) Colored state of pure Ni-O film
- 2) Bleached state of pure Ni-O film
- 3) Colored state of Ni-O film cont Co
- 4) Bleached state of Ni-O film cont Co

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3.3 Electrochemical Properties

The electrochemical information was obtained by studying the cyclic voltammetry, a. c. impedance and anodic polarization characteristics of the NiO_xH_y film on the Ni plate.

1) Cyclic Voltammetry

Linear potential scan experiments were carried out under the sweep rates of 2 ~ 36 mV/s in the range of - 0.6 ~ 0.7 (vs. HgO/Hg). The switching phenomenon involving coloration and bleaching of the NiO_xH_y corresponds to their anodic and cathodic processes, which has been proved with the result of in situ spectroscopic studies by Yu P C.^[2]

Fig. 4 shows the cyclic voltammogram of pure and composite NiO_xH_y film at the sweep rate of 2 mV/s. Just as the effect upon the positive electrode in alkaline batteries, the addition of the Co lowers the working potentials. They make the oxidation peak position decrease from 457 to 404 mV and make the reduction peak position decrease from 369 to 310 mV. Obviously the color switching voltage is lowered due to the addition of Co, but the difference between the oxidation and reduction peak position changes a little, meaning the effect on the reaction reversibility was small.

It is known that the diffusion of the proton is the rate determining step of the redox reaction^[12,13]. The solution of the current-velocity relationship for a potential scan is always written as:

$$i_p = 2.69 \times 10^5 \cdot n_e^{3/2} \cdot D^{1/2} \cdot C^0 \cdot v^{1/2} \quad (2)$$

where i_p is the peak current density during a

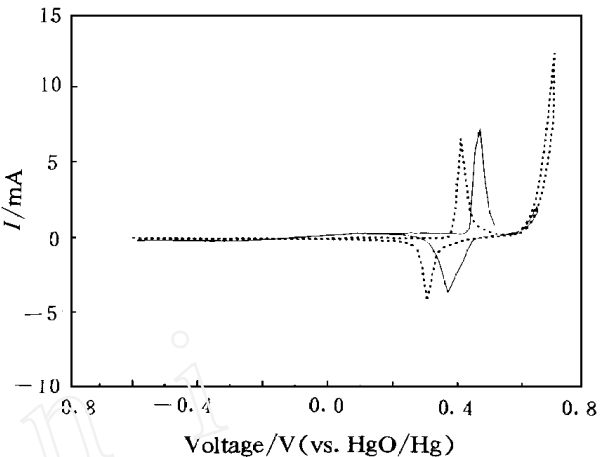


Fig. 4 Cyclic voltammogram of the pure and composite NiO_xH_y films on Ni substrate at 2 mV/s

— Pure Ni-O film
 - - - Composite Ni-O film

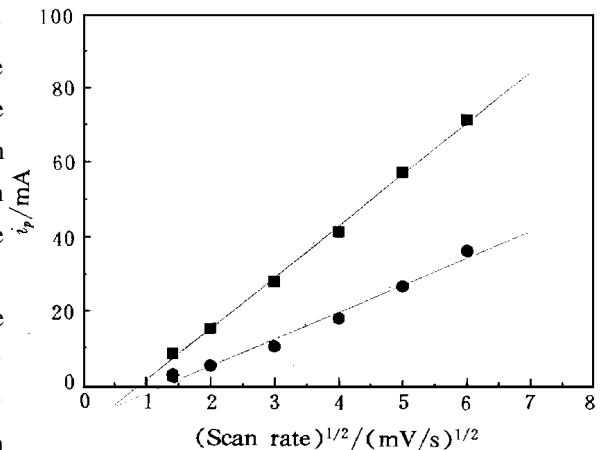


Fig. 5 Plots of oxidation peak current vs. (sweep rate) for the films on Ni substrate
 ● pure Ni-O film; ■ Ni-O film cont. 16.2% Co

potential scan at 25 mV/s as a function of scan rate $v^{1/2}$ and C^0 is the initial concentration of reactant. According to this solution, a linear relationship is to be found in the plot of the peak current density i_p versus the square root of the sweep rate $v^{1/2}$, as shown in Fig. 5. The values of C^0 was taken from the paper of Mac Arthur D M^[13] and the n_e is regard as 1. The result is 5.74×10^{-11} cm²/s for the pure NiO_xH_y and 2.66×10^{-11} cm²/s for the composite one. Therefore, the 16.2% Co has a negative effect on the reaction kinetics.

2) A. C. Impedance

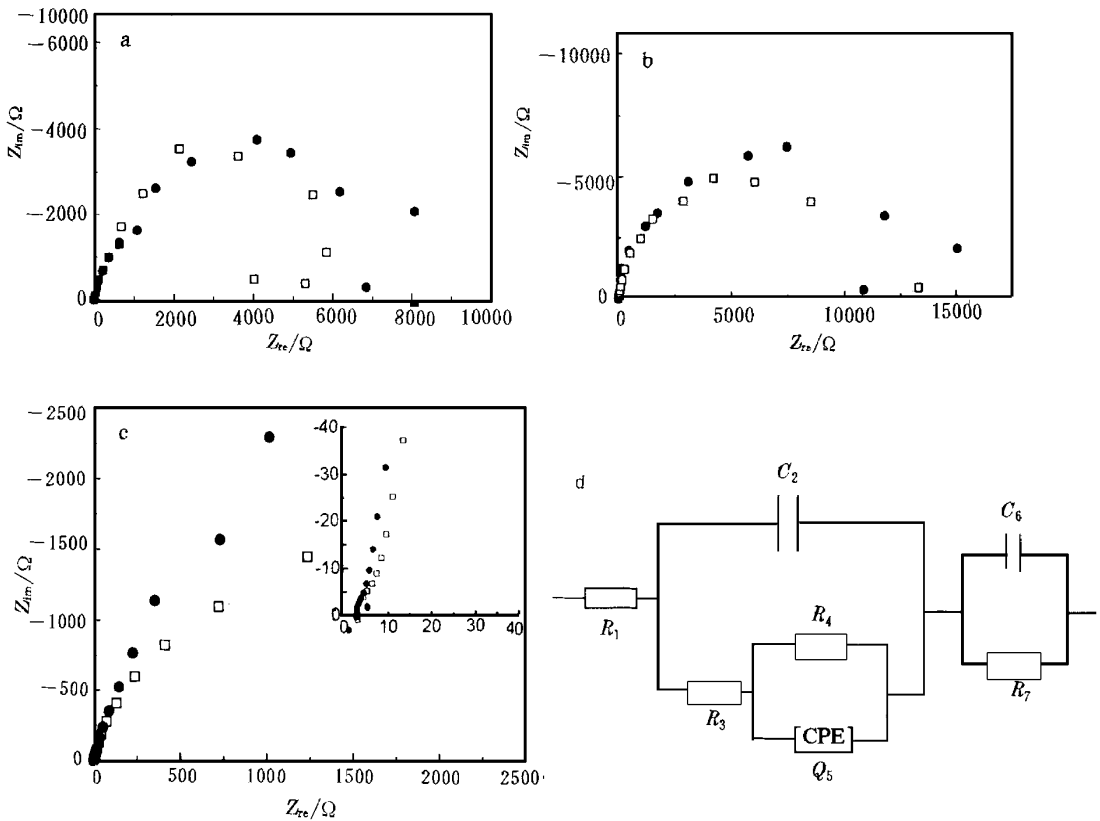


Fig. 6 Sluycers diagrams of the pure and composite NiO_xH_y films at different potential

- a) 0 mV ; b) 250 mV ; c) 500 mV , \square , pure N-O film; \bullet , Composite N-O film
- d) The equivalent circuit for the films at 500 mV

The impedance measurements of the pure and composite NiO_xH_y film on Ni plate were carried out respectively at the potential of 0 , 250 and 500 mV successively , corresponding to the process of coloring. Fig 6a ~ 6c present the real and imaginary components in the complex plane for each frequency of the two kinds of electrodes at difference applied potentials. Under the initial 0 mV , the impedance spectra of them are similar : at high frequencies , the data show a capacitive arc , and in low frequency range , an inductive component is observed on both impedance plane.

Compared with the pure Ni-O film, the arc of the composite one is bigger at the high frequencies. As the potential rose, the inductive components are fading away. Being oxidized to 500 mV, the impedance spectra of the both electrodes are composed of a capacitive arc and also a small semicircle in high frequency part, as shown in Fig 6c. The small semicircle is due to the charge transfer process, and the big capacitive arc relates to the diffusion effect. Because of the "finite diffusion length effects" which resulted from the film electrode, the diffusion element changed from a 45° straight line to a part of an arc. The corresponding equivalent circuit is shown in Fig 6d. R_4 in parallel with Q_5 can be regarded as the Warburg element. The values of the circuit elements are listed in Table 1. These values are extracted by means of EQUIVCRT software. Considering these results, it can be concluded that the addition of 16.2 % Co has some negative effect on the coloring kinetic process.

Tab. 1 Values of the circuit elements for the electrodes being anodized at 500 mV

Co/at %	$R_1/$	C_2/ F	$R_3/$	$R_4/$	Q_5/ F	n_5	C_6/ F	$R_7/$
0	2.94	3.18×10^{-3}	42	3.45×10^3	2.25×10^{-3}	0.97	2.23×10^{-3}	4.1
16.2	3.09	3.94×10^{-3}	144	1.18×10^4	1.54×10^{-3}	0.72	3.56×10^{-3}	3.0

3) Polarization Curves for OER

Fig. 7 shows the anodic polarization curves for OER (oxygen evolution reaction) on the NiO_xH_y film in 1 mol/L KOH. It can be seen obviously that when the polarization potential is below 850 mV (vs. HgO/Hg), the current of the NiO_xH_y film containing Co is lower than that of the pure one under the same potential, which means the addition of 16.2 % Co can raise the oxygen evolution potential V_{O_2} . As we have known, the Co can also decrease the oxidation potential V_{ox} , so the difference between V_{ox} and V_{O_2} is enlarged. Because the oxidation of the active material and the evolution of oxygen are competitive reactions and usually occurred at the same time when the oxidizing current is high, the coloration efficiency of the NiO_xH_y film at a high oxidizing rate will be increased. Meanwhile, the decrease of the oxygen evolution

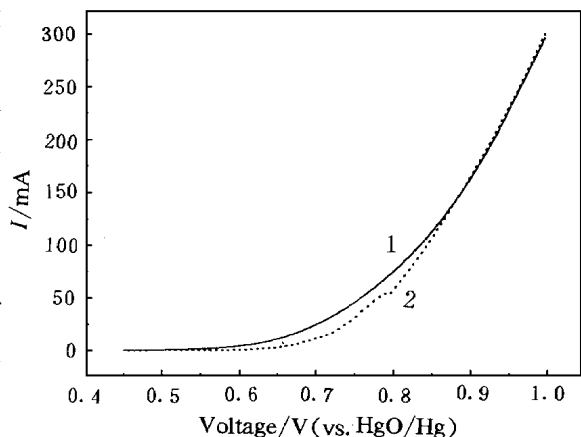


Fig. 7 The anodic polarization curves of the pure and composite NiO_xH_y film on Ni substrate

- 1) Pure NiO_xH_y film
- 2) NiO_xH_y cont 16.2 % Co

can prevent the electrochromic device using aqueous media from leakage to a certain degree. Both of the two effects are very favorable to the electrochromic material. When the potential is high than 850 mV, the anodic polarization characters of the two kinds of NiO_xH_y film are very similar, but that doesn't matter, because such high voltages are seldom used.

4 Conclusions

- 1) The difference of visible transmittance T of the Ni hydroxide film on ITO glass was increased by the addition of Co. For the film on Ni plate, the Co increased the reflectance difference R in NIR area.
- 2) The additions of Co lower the working potential of the Nickel hydroxide film, but have a little negative effect on the coloring reaction kinetics.
- 3) The presence of Co can raise the potential of oxygen evaluation.

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Co 对 NiO_xH_y 薄膜电致变色性能的影响

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摘要 本文利用阴极化电沉积法在抛光镍板及 ITO 玻璃表面制备了含 Co 量为 16.2% 的 NiO_xH_y 薄膜,薄膜厚度分别为 42 nm、21 nm,采用透射光谱以及线性电位扫描、交流阻抗和阳极稳态极化曲线等测试技术,考察了 Co 对 NiO_xH_y 薄膜电致变色性能的影响,光谱测试范围为 300 ~ 2 500 nm. 结果发现:Co 能降低薄膜着色态在可见光区及部分近红外区的透过率,通过电压调节不仅可以调光而且可望能够控温;同时 Co 还能降低 NiO_xH_y 薄膜电致变色电位,升高薄膜氧化着色过程中的氧析出过电位,对薄膜的电致变色性能有改进作用,但降低了着色过程中质子的扩散系数.

关键词 电致变电, NiO_xH_y 膜, Co