Vacancy dependent electrochromic behaviors of NiO$_x$ anodes: As a single layer and in devices

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ABSTRACT

Electrochromic(EC), nonstoichiometric NiO$_x$ thin films were made by reactive magnetron sputtering at low oxygen flow ratio(i.e., P = O$_2$/Ar + O$_2$ ≤ 10%). The results of optical spectral, x-ray diffraction spectrum, and x-ray photoelectron spectroscopy analyses indicate that the samples are oxygen(nickel)-deficient as P ≤ %4(≥%6), resulting in sub(over)-stoichiometry films. Spectroelectrochemical measurements show that the EC effect of NiO$_x$ in nonaqueous PC − LiClO$_4$ electrolyte is direct correlation with the nickel vacancy concentration in films, while that in the aqueous KOH solution is nearly uninfluenced upon the change in stoichiometry as P ≥ %4. The films deposited at P = 6% exhibit higher coloration efficiency of − 25.3 cm^{2}C^{-1}, larger ionic diffusion coefficient of − 2.84 × 10^{-14} m^{2}s^{-1}, and broader EC modulation span of 24% in PC − LiClO$_4$ than the other ones. Based upon these values, EC devices featuring a WO$_3$/PMMA − PC − LiClO$_4$/NiO$_x$ structure and excellent performances were fabricated. We demonstrated that the nickel anodization should be responsible for the initial "activation" phenomena, which decreases(increases) the number of oxygen(nickel) vacancies. Moreover, the cause of degradation resulting from Li$^+$-ion trapping in the IS layer was also clarified. This work provides a general framework for studying and designing superior EC devices, experimentally as well as theoretically.

1. Introduction

Materials are electrochromic [1,2], when their switching of redox states generate new or different electronic absorption bands in visible region. EC metallic oxides can show many different types of crystallinity depending on the preparation conditions, and the corner- and edge-sharing octahedra(a centrally positioned metallic atom surrounded by six oxygen atoms) cause a propensity for defects [3,4]. Over the past few decades, EC devices made of these materials are highly attractive in both the basic and applied research communities for their unusual spectroelectrochemical properties and immense potential applications [5–7]. Conventionally complementary EC device is constructed with ITO/EC/IC/IS/ITO, where EC, IC and IS are, respectively, electrochromic layer(cathodic colored materials), ion conductor layer (electrolytes) and ion storage layer(anodic colored materials) [8–10]. By applying a voltage between the transparent electrodes(In$_2$O$_3$: Sn, known as ITO) [11], the small positive ions[M$^+$, H$^+$ or Li$^+$] can be shuttled between the EC and IS layer leading to the reversible modulation of optical behaviors. It is commonly accepted that the properties

enhancements of metal oxide materials can be achieved by optimizing their stoichiometry, and the EC performances of device are intimately related with the types of electrolytes [8,12–37].

The physical nature of the EC mechanism for W oxide can be elucidated by the double–charge–injection model [12], namely

$$W^{VI}O_3|_{Bleached} + x[M^+ + e^-] \rightleftharpoons M_xW_y^{IV}W_z^VW_{1-x}^{VI}O_3|_{Colored}, \quad (1)$$
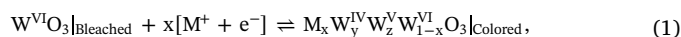
with the intercalated M$^+$/W atom ratio x = y + z < 1. Coloration is an electronic process, and the optical absorption originates from the intervalence charge transfer between the adjacent three kinds of sites W^{4+}, W^{5+}, and W^{6+} [8,12]. This model has successfully explicated the dependence of EC coloration efficiency on the defects and revealed the relationship between photochromic and electrochromic behaviors of sputtered tungsten oxide [13]. In contrast, the cause of the coloration for Ni oxide strongly depends on both cations and anions from the electrolytes, and it's working mechanism is still a matter of some controversy [14–17]. In the case of nonaqueous lithium perchlorate in propylene carbonate (PC − LiClO$_4$), by considering the interaction of
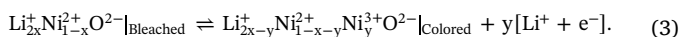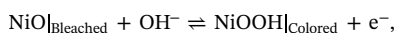
hydrogen with oxygen ions and water with nickel ions on grain surfaces [18], Campet et al. put forward a mechanism of an irreversible transformation between the surface(S) phase NiOOH and bulk(B) phase $Ni(OH)_2$ during the Li^+ ions insertion process [15]:

$$2xNiOOH|^S + (1 - 2x)NiO|^B + 2x[Li^+ + e^-] \rightarrow xNi(OH)_2|^B + Li_{2x}Ni_{1-x}O|^S. \tag{2}$$
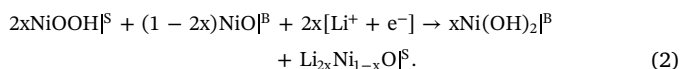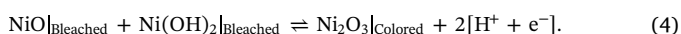
After that the absorption strength of Li-containing active materials on the surface can be further modulated by Li^+ insertion/extraction associated with reversible charge-transfer process between Ni^{2+} and Ni^{3+}, as described by

$$Li_{2x}^+Ni_{1-x}^{2+}O^{2-}|_{Bleached} \rightleftharpoons Li_{2x-y}^+Ni_{1-x-y}^{2+}Ni_y^{3+}O^{2-}|_{Colored} + y[Li^+ + e^-]. \tag{3}$$

This mechanism indicates that the absorption strength is governed by the nickel vacancy concentration in active materials. However, it appears insufficient to account for net EC effect in NiO_x, particularly for the sub-stoichiometry films with few Ni^{3+} species. While the evolving chemical nature of NiO_x, during EC process in aqueous potassium hydroxide(KOH) solution, is much more complicated. According to the extended Bode scheme [16,17], the initial hydration of Ni oxide toward hydroxide and oxy-hydroxide phases proceeds gradually through a combination of coloration from hydroxyl(OH^-) and bleaching through proton(H^+) according to

$$NiO|_{Bleached} + OH^- \rightleftharpoons NiOOH|_{Colored} + e^-,$$

$$Ni(OH)_2|_{Bleached} \rightleftharpoons NiOOH|_{Colored} + [H^+ + e^-],$$

and

$$NiO|_{Bleached} + Ni(OH)_2|_{Bleached} \rightleftharpoons Ni_2O_3|_{Colored} + 2[H^+ + e^-]. \tag{4}$$

Niklasson, suggested that the reversible charge-transfer between Ni^{2+} and Ni^{3+} is associated solely with proton after the "hydrogenation" process, with the oxygen content in the films being equal under different transmittance states [19].

Given the researches above, it seems quite evident that there is a tight correlation between EC behaviors and deficient stoichiometries in NiO_x films. Accordingly, the purpose of this paper is threefold: to investigate the optical characteristics, crystalline structure and chemical composition of the deposited NiO_x films upon changing from metallic nickel to oxide compound; to give a detailed study of the spectro-electrochemical properties of non-stoichiometry NiO_x in both aqueous and nonaqueous electrolytes; to fabricate all-solid-state devices using PMMA-based Li^+ as the conducting electrolyte, and further discuss it's evolution and degradation mechanisms.

2. Sample preparation and characterizations

Thin films of Ni/W oxide with thickness $\sim$ 260 nm were deposited by magnetron sputtering using a metallic Ni/W target (99.9%) with 100 mm diameter in Ar (99.99%) and O_2 (99.99%) ambient at room temperature. During the deposition process, the power and working pressure were set as 220/200 W and 3.0/2.2 Pa, respectively. The $O_2/Ar + O_2$ adjusted by mass flow controllers was varied from 0% to 10% for the deposition of Ni oxide thin films, while that for W oxide case was maintained at 75%. Base pressure of the sputter main chamber was under 1.6×10^{-3} Pa. The substrates were ITO-coated glass with a sheet resistance of 17 Ω/square and quartz glass(for optical measurements), which were successively chemically and ultrasonically cleaned for 20 min before deposition. The water-cooled targets to substrate spacing was kept at 7 cm, with an incident angle 41°, and the targets were pre-sputtered with the chosen working gases mixture in order to reach a steady state.

EC devices were constructed by separating complementary pairs of EC films with a polymer electrolyte. In the polymer electrolyte, a blend of Polycarbonate(PC) and polymethylmethacrylate(PMMA) was used as a host polymer and $LiClO_4$ as a dopant. The fabrication procedure is briefly described below: Magnetic stirring the mixed solution of PC and $LiClO_4$ with specific concentration ratio until complete dissolution, then dried in an oven at 80 °C resulting the formation of PMMA-based Li^+ ions containing electrolytes; Substrate I(glass/ITO/WO_3) and II (glass/ITO/NiO_x) were pressed onto the two sides of PMMA-based electrolyte and then installed into high-pressure autoclave for final assembly in high temperature. Detail of the fabrication can be found in the early report [20].

High-resolution FEI-Phillips XL30 S-FEG scanning electron microscope(SEM) was employed to measure the surface morphology of the NiO_x films. Prior to imaging by SEM, the films were sputter-coated with 10 nm gold for improving their conductivity. The structure and crystallinity were characterized by X-Ray Diffraction(XRD) on a Rigaku D/Max 2200 diffractometer with Cu $-$ Kα($\lambda = 1.5406$ Å) radiation source. Diffraction patterns were obtained for 2θ in the region $20° - 85°$ with a stepsize of 0.04°. The composition and chemical bonding states were measured by X-ray Photoelectron Spectroscopy(XPS, Physical Electronics PHI-5600 system) using an Al Ka X-ray source. Survey-scan spectra were acquired using a 187.85 eV pass-energy at a step of 0.1 eV, while for C-1s, O-1s and Ni-2p individual high-resolution spectra were taken at a pass-energy of 23.5 eV with 0.05 eV energy step. The $Ni - 2p_{3/2}$ and O-1s spectra were curvefitted employing a 30:70 Gaussian: Lorentzian peak shape with a Shirley-type background using the CasaXPS(version 2.1.16) software package.

Spectroelectrochemical studies were performed using a UV-visible-NIR spectrometer(Evolution 100, Thermo Electron Corporation) and a CHI660C electrochemical working station (Chenhua, Shanghai, China) equipped with three-electrode electrochemical cell. The electrochemical cell(positioned between the light source and the detector in the chamber of spectrometer) was employed Pt rod as the counter electrode, Ag/AgCl as the reference electrode and NiO_x film on ITO-coated glass substrate as the working electrode. The electrochemical tests for device were performed in a two-electrode configuration, and the reference was shorted with counter electrode. The cell filled with 1 M $PC - LiClO_4$/KOH electrolyte was used as the basic reference for the in situ optical response measurements of NiO_x films at $\lambda = 550$ nm, while that for the device with respect to air.

3. Results

The transmittance spectra in the range of 200–2000 nm and photographs of NiO_x films deposited at P varied form 0–10% in the gas mixture are shown in Fig. 1. Significant dependency of the color of the films on oxygen content is observed, switching from silvery white (P = 0%), dark(P = 2%) to opaque light brownish(P $\geq$ 4%) in different degrees, due to the evolution of stoichiometry and types of defects [10,21–23]. With P increased from 0–10%, it is observed that the ultraviolet absorption edge is observed to be blue-shifted first(P < 6%) for the decreased metallic nickel defects, then behaves red-shift(P $\geq$ 6%) for the increased nickel vacancies. Quantitative analysis were evaluated by the average transmittance $T_{Average} = \int f(\lambda)T(\lambda, P)d\lambda / \int f(\lambda)d\lambda$, where $f(\lambda)$ is the spectral sensitivity of the light-adapted eye and $T(\lambda, P)$ refer to the spectra transmittance [24]. Absorption of ultraviolet (UV, 200–420 nm) region by both glass and air is responsible for the reduced average transmittance value. In the visible (Vis, 420–780 nm) region, the average transmittance value is 0.5%, 18.1%, 71.6%, 61.7% and 53.0% for the films deposited at P = 0%, 2%, 4%, 6%, 8% and 10%, respectively. Because of the oxygen content sensitive, the optical transmittance in near-infrared (NIR, 780–2000 nm) region increases dramatically in the range of 0% < P $\leq$ 4%, while it has minor change as P $\geq$ 6%. Optical band gaps ΔE were calculated from the transmittance data by using Tauc's plot: $\alpha h\nu = A(h\nu - \Delta E)^m$, with the absorption coefficient α and exponent parameter m = 0.5/2 for direct/indirect transitions [27]. The dependence of band gap on the oxygen pressure is not systematic: the ΔE initially increases from 3.11 to 3.85 eV with the increase of P from 2% to 6%, due to the fall in the density of oxygen