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Electrochromism in nickel oxide and tungsten oxide thin films: Ion intercalation from different electrolytes

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Abstract

Electrochromic NiO₂ and WO₃ thin films were prepared by sputtering and were used in a feasibility study aimed at investigating mixtures of these two oxides. The object was to identify a suitable electrolyte, compatible with both NiO₂ and WO₃. To that end we carried out cyclic voltammetry in potassium hydroxide (KOH), propionic acid, and lithium perchlorate in propylene carbonate (Li-PC). WO₃ could be coloured in propionic acid and Li-PC, while NiO₂ could be coloured only in KOH. Both films showed best stability in Li-PC, which hence is well suited for further studies of mixed NiO₂ and WO₃.

Keywords

Electrochromism, nickel oxide, tungsten oxide, cyclic voltammetry, spectrophotometry

1. Introduction

Nickel oxide (NiO₂) and tungsten oxide (WO₃) are well known electrochromic (EC) materials [1]. EC materials change their optical properties during electrochemical oxidation and reduction through ion insertion. There are two kinds of EC materials: cathodic (colouring upon ion insertion) and anodic (colouring upon ion extraction). WO₃ is cathodic and turns blue when ions are inserted while NiO₂ is anodic and turns brown when ions are extracted. The materials bleach if the processes are reversed. Different electroactive ions can be used; however small sized ions are preferred for the insertion chemistry. This work evaluated H⁺ and Li⁺ insertion cations.

Both NiO₂ and WO₃ are widely used for EC applications such as in smart windows [2]. A smart window consists of a number of layers: EC thin films (one anodic and one cathodic), electron conductive layers and an ion containing electrolyte. When a potential is applied over the smart window, ions in the electrolyte are transported between the EC layers and the transparency changes. In recent years materials development in this field has frequently been directed to the study of mixed oxides [3-6]. These promising materials may show improved optical, electrochemical and stability properties, as compared to the corresponding properties of the constituent oxides. From a fundamental point of view, mixing a cathodic material (such as WO₃) and an anodic one (such as NiO₂) is of considerable interest. Hence the objective of this work was to find a common electrolyte for thin films of WO₃ and NiO₂ to enable future studies of mixtures of the two oxides over the whole concentration range. Three electrolytes of different categories were investigated: protic and basic 1 M potassium hydroxide (KOH), protic and acidic 0.1 M propionic acid, and aprotic and Lewis acidic 1 M lithium perchlorate

in propylene carbonate (Li-PC). The choice of an appropriate electrolyte is complicated by the fact that NiO_z is sensitive to acids and that WO_y is sensitive to bases. Furthermore, electrochemical cycling of NiO_z in Li-PC is rather poorly known and only a few studies have been published [7,8].

Section 2 describes the experimental methods. The films were prepared by sputtering and were characterized by a number of techniques. The electrochemical properties were examined by cyclic voltammetry and the optical properties by spectrophotometry in the visible range. Section 3 presents results on the influence of the electrolytes on the electrochemical properties such as current density and charge capacity, and the optical properties such as transmittance and colouration efficiency. Structure, grain size, composition, and density are reported for the NiO_z and WO_y films. Results are also given for WO_y/liquid electrolyte/NiO_z devices in order to verify the data on the individual thin films. Finally, section 4 presents the conclusions.

2. Experimental methods

Thin films of NiO_z and WO_y were prepared by reactive dc magnetron sputtering in a deposition system based on a Balzers UTT 400 unit. Depositions took place onto unheated glass plates, 5 x 5 cm² in size, precoated with transparent and electron conductive In₂O₃:Sn (ITO). Some films were made also on substrates of C and Si. The films were deposited in an argon/oxygen atmosphere with an O₂/Ar mass flow ratio of 2 % for NiO_z and 13 % for WO_y. These ratios were chosen for optimal transparency of the as-deposited films. Previous work has shown that the EC properties are superior if the as-deposited films have maximum transparency [9-12]. The total pressure during thin film manufacturing was ~ 30 mTorr, and the discharge power was 230 and 250 W when depositing WO_y and NiO_z, respectively. The film thickness was ~300 nm as measured by profilometry.

The structure and grain size of the films were determined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer operating with CuK_α radiation at a wavelength of 1.54 Å. The grain size *D* was determined from Scherrers formula [13],

$$D = (k \cdot \lambda_x) / (\beta \cdot \cos \theta) \quad (1)$$

where *k* is the shape factor, λ_x is the X-ray wavelength, β is the full width at half maximum of the X-ray diffraction peak, and θ is the diffraction angle.

Composition and density were determined by Rutherford backscattering spectroscopy (RBS) applied to films deposited onto C substrates. The measurements were carried out at the Uppsala Tandem Laboratory, using 2 MeV 4He ions backscattered at an angle of 167°. The RBS data were fitted to a model of the film–substrate system by use of the program SIMNRA [14], from which the composition and the atomic concentration were found.

XPS used a PHI Quantum 2000 Scanning ESCA Microprobe operating with monochromated Al K_α radiation and a pass energy of 46.95 eV. The XPS measurements were only performed at the surface of the sample, i.e. no presputtering was done. The presence of W4f, Ni2p, O1s and C1 was investigated and the atomic concentration was achieved by fitting a Gauss-Lorentz curve to the spectra.

Electrochemical and optical properties were investigated for the various thin film materials and electrolytes. Cyclic voltammetry (CV) showed alterations of current density and charge capacity of the film in the chosen potential region. Optical measurements indicated changes in spectral transmittance modulation within the $380 < \lambda < 800$ nm wavelength range upon variations of the potential. These electrochemical and optical measurements were combined to determine the colouration efficiency (CE) between the coloured and the bleached state. CE is defined as the change in optical density (OD) per unit of inserted charge (Q), *i.e.*

$$CE = \Delta(OD)/\Delta Q \quad (2)$$

A high CE provides a large optical modulation for a small amount of charge, which is desirable for smart window applications. If the changes in reflectance between the bleached and coloured states are negligible, the CE can be obtained by

$$CE = (\ln(T_{Bleached}/T_{Coloured})) / (\Delta Q) \quad (3)$$

where $T_{Bleached}$ and $T_{Coloured}$ denote transmittance in bleached and coloured states, respectively, and ΔQ is a mean value of the exchanged charge needed to achieve the optical modulation.

In the CV measurements the electrodes were oxidized and reduced in a three electrode electrochemical cell. The electrochemical instrumentation embodied a computer controlled ECO Chemie Autolab/GPES interface. A scan rate of 10 mV/s was utilized in all experiments. The films were electrochemically cycled in three different electrolytes: 1 M KOH, 0.1 M propionic acid, and 1 M Li-PC. When using KOH and propionic acid the counter electrode was platinum and the reference electrode was Ag/AgCl. For the case of Li-PC, both counter and reference electrodes were Li foils. All potential values are given versus the standard hydrogen (SHE) potential. Li is reactive if exposed to air and moisture and hence all experiments with Li-PC were carried out inside an argon filled glove box. The number of inserted ions per NiO_x or WO_y unit, after stabilization, was calculated from

$$x = (Q \cdot M) / (e \cdot A \cdot d \cdot \rho \cdot N_A) \quad (4)$$

Here Q was taken as an average of inserted and extracted charge (if those were different). M is molar mass, e is elementary charge, A is intercalated/deintercalated area, d is film thickness, N_A is Avogadro's constant, and ρ is film density.

The optical measurements were carried out *in situ* during electrochemical cycling with a fibre optic spectrophotometer from Ocean optics. The entire electrochemical cell was put between a tungsten halogen lamp and a detector, as depicted in Fig. 1. When the film was cycled in KOH or propionic acid, the counter electrode was put opposite to the reference electrode. The transmittance was measured at $\lambda=500$ nm for the whole cycle. One cycle means that the EC film goes from fully bleached to fully coloured and then back again. The transmittance was also recorded at fully coloured and bleached states for $380 < \lambda < 800$ nm. The optical measurements were always made after pre-cycling for about ten cycles to ensure the reversibility of oxidation/reduction. The 100 % level

was taken as the transmittance of the cell containing only the liquid electrolyte. A two-terminal measurement was performed in the experiments with WO_y /liquid electrolyte/ NiO_x devices. The 100 % level was then set as the transmittance of the empty glass cell.

Figure 1: Schematic of the set-up for combined optical and electrochemical measurements. Current and voltage are denoted I and V , respectively. The glass cell was filled with electrolyte and the electrodes positioned with a distance of ~ 1.5 cm between the working and counter electrode. The whole electrochemical cell was put between a tungsten halogen lamp and a detector for optical measurements.

3. Results

3.1 Tungsten Oxide

The WO_y thin films were characterized by XRD, RBS and XPS. XRD showed no diffraction peaks, *i.e.* the WO_y films were amorphous. RBS yielded that the films were characterized by $y \sim 3.1 \pm 0.1$ and the density was about 5.2 g/cm^3 . XPS compositions were found to be uncertain because of organic residues on the surface.

In CV measurements on WO_y , only 0.1 M propionic acid and 1 M Li-PC could be used since 1 M KOH etched away the film almost immediately. The first scan in the CVs started at the equilibrium potential and the electrochemical ranges were optimized regarding reversibility and chemical reactions. The potential ranges were -0.3 to 0.6 and -1.0 to 0.8 V vs SHE in propionic acid and Li-PC, respectively. Attempts to improve the charge capacity in propionic acid by increasing the negative potential limit resulted in irreversible reduction of the material. In propionic acid the films obtained a milky appearance after ~ 30 cycles. The charge capacities for WO_y were 26.0 and 5.2 mC/cm^2 in 1 M Li-PC and 0.1 M propionic acid, respectively. The difference is probably due to the use of different potential ranges or ensued from the intercalation of Li^+ ions being easier. For the chosen potential ranges, the x -values were 0.07 (H^+/WO_y) when using propionic acid and 0.36 (Li^+/WO_y) when using Li-PC.

Fig. 2 (a) and (b) show changes of the transmittance at $\lambda = 550 \text{ nm}$ during intercalation of H^+ and Li^+ , respectively. The film was initially transparent and, as the potential was lowered, reduction occurred and the films were coloured. When the lower potential limit was reached, the potential scan was reversed and the film was oxidized, *i.e.*, emptied of inserted ions, and bleached. The optical modulation was larger for films cycled in Li-PC

than in propionic acid, as can be seen in Fig. 3. However, the colouration efficiency was almost the same for the film cycled in propionic acid and in Li-PC, at least for $380 < \lambda < 800$ nm.

Figure 2: Current density and optical transmittance at 550 nm for WO_3 measured *in situ* upon electrochemical cycling at 10 mV/s in (a) 0.1 M propionic acid and (b) 1 M Li-PC. The reference for the optical measurement is the glass cell containing the liquid electrolyte.

Figure 3: Spectral transmittance for WO_3 cycled in 1 M Li-PC and 0.1 M propionic acid. Data are shown for bleached and coloured states. The reference for the optical measurements is the glass cell containing the liquid electrolyte.

3.2 Nickel Oxide

Fig. 4 shows an XRD pattern for a NiO film. The peaks were assigned to the cubic phase of NiO [15]. The XRD spectrum indicated that the NiO_x film was polycrystalline and had a grain size of about 26.5 nm, calculated by equation 1. RBS showed that z was about 1.3 and the density ρ about 3.9 g/cm^3 . The composition was consistent with XPS measurements. By examining the carbonate contribution to C1 at 289 eV by XPS it was concluded that about 10% of the oxygen was bound to carbon. The films are probably not pure NiO_z , but also contain hydroxide phases, as shown by Avendano et al. [16].

Figure 4: XRD spectrum for NiO_x deposited on Si.

NiO_x was compatible with all three electrolytes. The first CV scan started at the equilibrium potential, and the electrochemical ranges were optimized regarding reversibility and chemical reactions. The potential ranges were -0.3 to 0.8, +0.2 to 1 and -0.55 to 0.95 V vs SHE for cycling in KOH, propionic acid, and Li-PC, respectively. At the positive potential limit in Li-PC, some reaction occurred which resulted in a dramatic decrease in the oxidation peak; it was possibly due to passivation or some other deteriorating electrochemical reactions. The oxidation peak was enhanced if the oxidation limit was increased, which supports the hypothesis of surface passivation, possibly due to electrolyte oxidation and the formation of a surface layer. For propionic acid, a difficulty ensues from the fact that NiO_x is sensitive to acids, and an increased positive potential limit resulted in enhanced irreversibility and even removal of the film.

Voltammograms for NiO_x cycled in different electrolytes are given in Fig. 5 (a) and (b). Large differences were observed among the voltammograms: specifically, the oxidation and reduction peaks increased in KOH during cycling, while the opposite was found in the two other electrolytes. The increasing peaks in KOH might be due to the formation of NiO_xH_w on grain or pore surfaces [17]. The charge capacity for NiO_x was 14.5 mC/cm^2 in KOH, 1.2 mC/cm^2 in Li-PC and 1.5 mC/cm^2 in propionic acid. Evidently the charge capacity is much higher for films cycled in KOH than in Li-PC and propionic acid. For the chosen potential ranges and after stabilization, the x -values were ~ 0.1 (H^+/NiO_x), 0.01 (H^+/NiO_x), and 0.008 (Li^+/NiO_x) when using KOH, propionic acid, and Li-PC, respectively.

The collected evidence is that another kind of electrochemistry is involved when NiO_x is exposed to KOH than to the two other electrolytes, *i.e.*, the pH-value seems to be important for the NiO_x reaction. The Pourbaix diagram for Ni verifies that this metal is stable at high pH and that corrosion occurs for low pH [18]. French et al [19] discovered that in LiOH the H^+ inside the film deintercalate to combine water together with OH^- and that it is this reaction that causes the ion movements. This agrees with the work of Avendaño et al [17] that showed that protons were the ones responsible for the induced current density. So even if no free H^+ exists in the KOH electrolyte, protons are still the dependable ions. In propionic acid and Li-PC on the other hand it seems that no charge is getting extracted from the as-deposited film itself, *i.e.* H^+ and Li^+ inside the electrolyte are the ones causing the optical modulation. The applied potential is obviously not powerful enough to deintercalate ions from the films itself. In KOH on the other hand the H^+ seems to get a lot of help from the OH^- .

Figure 5: Cyclic voltammograms for NiO_2 cycled in (a) 0.1 M propionic acid and 1 M Li-PC, and (b) KOH. The scan rate was 10 mV/s and the five different sweeps correspond to cycle number 1, 2, 10, 20 and 30.

Fig. 6 (a), (b) and (c) show the evolution of the transmittance at $\lambda = 550$ nm during electrochemical cycling. The initial transmittance of the NiO_2 film was $\sim 85\%$. Immersing the film in KOH and sweeping towards higher potentials led to oxidation, *i.e.*, ions were extracted, and the film was coloured. When the positive potential limit was reached the potential scan was reversed and the film was reduced and bleached again. If the film was immersed in propionic acid or Li-PC the film was only bleached compared to the as-deposited state and hardly coloured at all, see Fig. 6.

Figure 6: Current density and optical transmittance at 550 nm for NiO_2 measured *in situ* upon electrochemical cycling at 10mV/s in (a) 0.1 M propionic acid, (b) 1 M Li-PC and (c) 1 M KOH. The reference for the optical measurement is the glass cell containing the liquid electrolyte.

Fig. 7 shows that the optical modulation was superior for NiO_2 cycled in KOH. For the applied potential ranges it was also observed that KOH only colours the film relative to the state of the as-deposited film, while Li-PC and propionic acid only bleach the film relative to the as deposited case. Even though the optical modulation was largest when using KOH, the colouration efficiency was larger for Li-PC and propionic acid, which gives a hint that the optical modulation would be improved if one could increase the charge capacity of the film in the latter electrolytes.

Figure 7: Spectral transmittance for NiO_x cycled in 1 M KOH, 1 M Li-PC, and 0.1 M propionic acid. Data are shown for the bleached and coloured states. The reference for the optical measurement is the glass cell containing the liquid electrolyte.

3.3 WO_y /liquid electrolyte/ NiO_z devices

The experiments reported above indicate that both Li-PC and propionic acid are usable electrolytes for NiO_z and WO_y . As verification, those electrolytes were used in WO_y /liquid electrolyte/ NiO_z devices. The charge capacity was measured to be 1.5 to 2 mC/cm^2 for both electrolytes. The low charge capacity indicates that the NiO_z film limits the amount of available charge. The x -values for the two films in the WO_y /liquid electrolyte/ NiO_z device were ~ 0.01 (H^+/NiO_z and Li^+/NiO_z) and ~ 0.03 (H^+/WO_y and Li^+/WO_y) for propionic acid and Li-PC, respectively.

Fig. 8 shows transmittance modulation at $\lambda = 550 \text{ nm}$ during electrochemical cycling. The difference between the transmittance in the coloured and bleached states for these simple devices is comparable to values given in the literature for solid-state devices [2, 20]. This is remarkable in view of the very low intercalation levels quoted above for the dark state of our model devices and suggests that there is room for considerable improvements of the optical contrast in state-of-the-art devices.

Figure 8: Current density and optical transmittance at 550 nm for a WO_y /liquid electrolyte/ NiO_z device cycled at 10 mV/s in (a) 0.1 M propionic acid and (b) 1 M Li-PC.

Fig. 9 shows that the optical modulation is larger for Li-PC than for propionic acid in the visible range. For that reason, and accounting for the fact that propionic acid resulted in more irreversibility and surface reactions, Li-PC was found to be the best suited electrolyte for devices made of NiO_z and WO_y .

Figure 9: Spectral transmittance for a WO_3 /liquid electrolyte/ NiO_2 device cycled in the indicated electrolytes. Data are shown for bleached and coloured states.

4. Conclusions

The two electrochromic materials NiO_2 and WO_3 were cycled in three different electrolytes, specifically being protic and basic 1 M potassium hydroxide, protic and acid 0.1 M propionic acid, and aprotic and Lewis acidic 1 M lithium perchlorate in propylene carbonate. WO_3 could be coloured in propionic acid and Li-PC while NiO_2 could be coloured only in KOH. Propionic acid and Li-PC allowed cycling of NiO_2 between an as-deposited and a very bleached state. The optical modulation of NiO_2 was superior in KOH. However the colouration efficiency for NiO_2 in KOH was only half of that for the other two electrolytes. Use of Li-PC and propionic acid resulted in similar magnitudes of the colouration efficiency for the NiO_2 and the WO_3 films. A comparison between the two films shows that the colouration efficiency for WO_3 is smaller at short wavelengths and rises up to the same value as that of NiO_2 at longer wavelengths, see Fig. 10.

Figure 10: Spectral colouration efficiency for WO_3 cycled in 1 M Li-PC and 0.1 M propionic acid, and colouration efficiency for NiO_2 cycled in 1 M KOH, 1 M Li-PC and 0.1 M propionic acid.

The conclusion for NiO_2 is that the difference between immersing the film in propionic acid and in Li-PC is very small, and that KOH is superior when it comes to optical modulation and charge capacity. For WO_3 , KOH could not be used at all and Li-PC was the electrolyte giving the best optical and electrochemical properties. Measurements on WO_3 /liquid electrolyte/ NiO_2 devices verified the previously mentioned results. Further considering the chemical problems related to propionic acid, such as irreversibility and

surface reactions, Li-PC stands out as the best of the investigated electrolytes for further investigations on the electrochromism in mixed nickel tungsten oxide.

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