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Electrochromic performance of Ni oxide thin films intercalated with Li⁺ ions

Rui-Tao Wen¹, Gunnar A Niklasson and Claes G Granqvist

Department of Engineering Sciences, The Ångström Laboratory, Uppsala University
P. O. Box 534, SE-75121 Uppsala, Sweden

E-mail: Ruitao.Wen@angstrom.uu.se

Abstract. Porous Ni oxide thin films were deposited on unheated ITO/glass substrates by sputtering in argon–oxygen. The as-deposited thin films have a cubic NiO structure and still exhibit such a structure after 10,000 electrochemical cycles in 1 M LiClO₄ in propylene carbonate in the range between 2.0 and 4.1 V vs Li/Li⁺. Electrochromic performance showed a rapid drop of charge density over the first hundreds of cycles and subsequently a very slow decrease. The charge density was 87% of the initial one after 1,000 cycles and 82% after 10,000 cycles, indicating an extremely slow decay after 1,000 cycles. Optical modulation was also slightly decreased after 10,000 cycles, which is due to the drop of charge density.

1. Introduction

Energy consumption in buildings is a very urgent issue, since the fraction of the world's primary energy that is used in buildings amounts to as much as 30–40% [1]. Traditional windows are often regarded as weak components for efficient energy control in buildings [2]. However, switchable windows, also known as smart windows [3], are very promising for alleviating the energy consumption effectively in buildings [4, 5]. Specifically, “smart” windows based on electrochromism can regulate the amount of sunlight that can pass through the window when an external, small potential is applied. Therefore, electrochromic (EC) thin films have attracted intensive interest and have been widely studied in recent years. The most important requirements for smart windows are large optical modulation in the solar spectrum and long-term durability.

Ni oxide is an anodic EC material and has great potential in smart windows. Most previous research work was performed on Ni oxide thin films in aqueous electrolyte systems (mostly potassium hydroxide, KOH) [3], and it was found that Ni oxide has large optical modulation [6], high coloration efficiency [7], good durability [8], and fast switching time [7]. In some cases, Ni oxide films also served as counter electrode to WO₃ [9] in EC windows in order to get increased optical modulation, since tungsten oxide darkens under charge insertion while Ni oxide darkens under charge extraction [10]. In addition, the color appearance is improved because the brown color of Ni oxide is complementary to the blue color of tungsten oxide, both together giving a neutral (gray) appearance in the colored state. However, tungsten oxide and Ni oxide are chemically incompatible when they are working in an acidic or alkaline aqueous electrolyte environment [11]. Therefore, Ni oxide needs to be compatible with tungsten oxide in a non-aqueous electrolyte system, where LiClO₄ in propylene

¹ Corresponding author: Ruitao.Wen@angstrom.uu.se



carbonate (Li-PC) is mostly used in WO₃-based EC devices. So far, a number of investigations have been published on EC performance of Ni oxide in non-aqueous electrolyte [12–14]. However, long-term durability of Ni oxide in Li⁺-based electrolyte has seldom been reported. In fact, the long-term stability is one of the most critical issues for commercial use of Ni-oxide-containing smart windows.

In this report, Ni oxide thin films of thickness ~300 nm were deposited on unheated substrates by reactive dc magnetron sputtering. The working pressure was kept high in order to obtain porous thin films [15]. EC properties were characterized by cyclic voltammetry (CV) and optical measurements.

2. Experimental

Film deposition — The Ni oxide films were deposited by reactive dc magnetron sputtering in a system based on a Balzers UTT 400 unit. The target was a 5-cm-diameter cylindrical plate of metallic nickel (99.95%). Sputtering was performed in an argon–oxygen atmosphere at room temperature. Pre-sputtering took place in argon (99.998%) for 5 minutes, and oxygen (99.998%) was then introduced. During deposition, the O₂/Ar gas-flow ratio was kept at a constant value of 3.5%. The total pressure during sputtering was set to ~30 mTorr, and the power at the target was 200 W. The substrates were glass plates pre-coated with transparent and electrically conducting layers of In₂O₃:Sn (known as ITO) with a sheet resistance of 60 Ω. Carbon substrates were also used to deposit films for Rutherford Backscattering Spectrometry (RBS) measurements. The substrates were rotated during deposition to ensure even films. The film thickness *d* was measured by surface profilometry using a DektakXT instrument.

Physical techniques — Crystalline structures were investigated by X-ray diffraction (XRD), using a Siemens D5000 diffractometer with CuK_α radiation at a wavelength of 0.154 nm. Structure and phase composition were obtained by comparison with the Joint Committee on Powder Diffraction Standards (JCDPS) data base. Morphology of the films was characterized by scanning electron microscopy (SEM) using a LEO 1550 FEG Gemini instrument with an acceleration voltage of 10 kV. Density and atomic concentrations of the films were determined by RBS at the Uppsala Tandem Laboratory, using 2MeV 4He⁺ ions back scattered at an angle of 170 degrees. The density was calculated from $(M \cdot N_s)/(n_a \cdot N_A \cdot d)$, where *M* is molar mass, *N_s* is areal density of atoms, *n_a* is the number of atoms in a molecule, and *N_A* is Avogadro's constant. The density was found to be ~4.2 g/cm³, indicating that the films are highly porous compared to bulk NiO (6.8 g/cm³).

Electrochemical and in situ optical characterization — CV was carried out in a conventional three-electrode electrochemical cell by use of a computer-controlled ECO Autolab/GPES Interface. Ni oxide served as the working electrode in an electrolyte of 1 M Li-PC. Both counter and reference electrodes were Li foils, and the potential scans were performed between 2.0 and 4.1 V vs Li/Li⁺ with a sweep rate of 50 mV/s. The low potential limit was set to 2.0 V in order to get an easy comparison with previous research on iridium oxide [16]. Optical transmittance was recorded *in situ* during electrochemical cycling of Ni oxide films in the 380–800 nm wavelength range by using a fiber-optical instrument from Ocean Optics. The electrochemical cell was positioned between a tungsten halogen lamp and the detector, and the 100%-level was taken as the transmittance before immersion of the sample in the electrolyte.

3. Results and Discussions

XRD patterns of as-deposited Ni oxide and the same film after 10,000 cycles are compared in figure 1. A spectrum of an ITO coated glass is also shown as a reference. The as-deposited Ni oxide film exhibits a cubic structure (*Fm3m*), as indicated by the (111), (200), (220), (311) and (220) lattice planes (black curve). No traces of phases containing hydrogen, or other phases, were detected. Grain size was calculated to be ~40 nm by Scherrer's formula [17] using the (111) diffraction peak. The sample still shows the cubic structure (red curve), and no other phase appears after electrochemical cycling for 10,000 times. By carefully comparing the diffraction peaks before and after cycling, we find that the crystallinity of Ni oxide is hardly altered after cycling, which is indicated by the same

diffraction intensity of the (111) peak (figure 1b). This means that the structure is still very stable after long-term cycling.

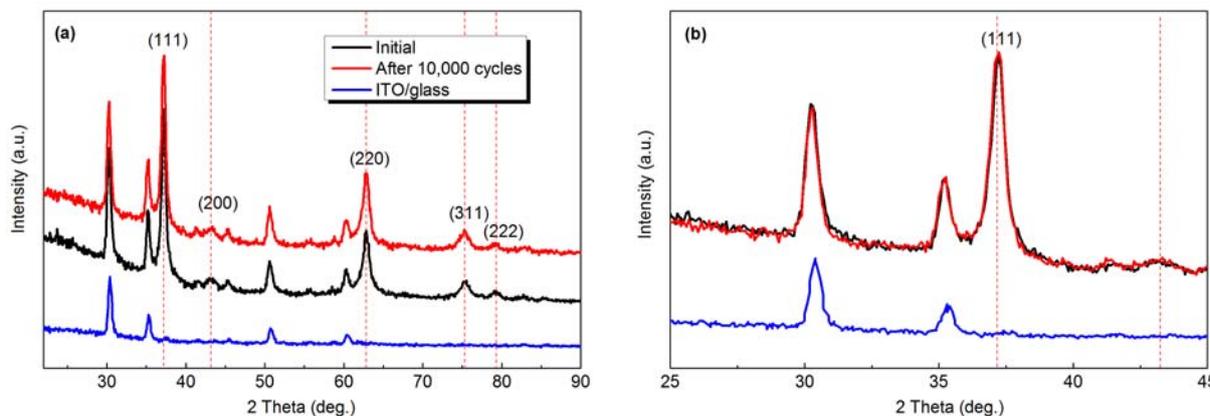


Figure 1. X-ray diffraction of Ni oxide films on ITO coated glass. Panel (a) refers to Ni oxide films before and after 10,000 cycles; peaks are assigned to the cubic phase of NiO (JCPDS No. 04-0835), as indicated by the red dash lines. Panel (b) is an enlargement of panel (a) between 25 and 45°. A diffractogram of the ITO coated glass is shown for comparison..

The surface morphology of the Ni oxide films before and after cycling was characterized by SEM, as illustrated in figure 2. The images show that the films are very homogeneous, and their surfaces have a triangular pyramid-like appearance with a characteristic length of ~ 40 nm. This result is consistent with the calculated grain size using Scherrer's formula. Clearly, the surface was almost unchanged after electrochemical cycling and still showed triangular pyramids.

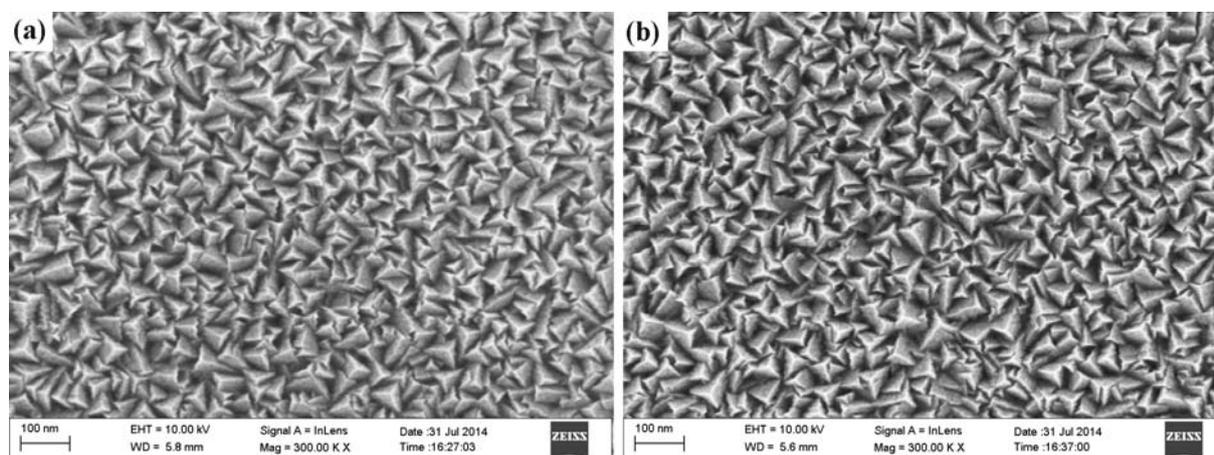


Figure 2. SEM images of Ni oxide thin films (a) before cycling and (b) after 10,000 cycles.

Figure 3 (a) shows CV curves for Ni oxide thin films cycled in 1 M Li-PC. It can be seen that charge insertion and extraction takes place in the whole potential range. There is a persistent shrinking of the CV curve during cycling, implying a decrease of charge insertion and extraction. To be specific, we also plot the inserted and extracted charge density *vs* cycle number in figure 3(b). A rapid drop of charge density can be observed during the first hundreds of cycles; then the charge density drops very slowly upon further cycling, indicating that Ni oxide is stable as an EC layer. *In situ* optical transmittance was recorded between 380 and 800 nm for Ni oxide films, as shown in figure 4. The bleached state was almost unchanged after 10,000 cycles and remained at $\sim 90\%$. However, the

colored-state transmittance was slightly increased. The variation of optical transmittance is in agreement with the decrease of charge density after long-term cycling.

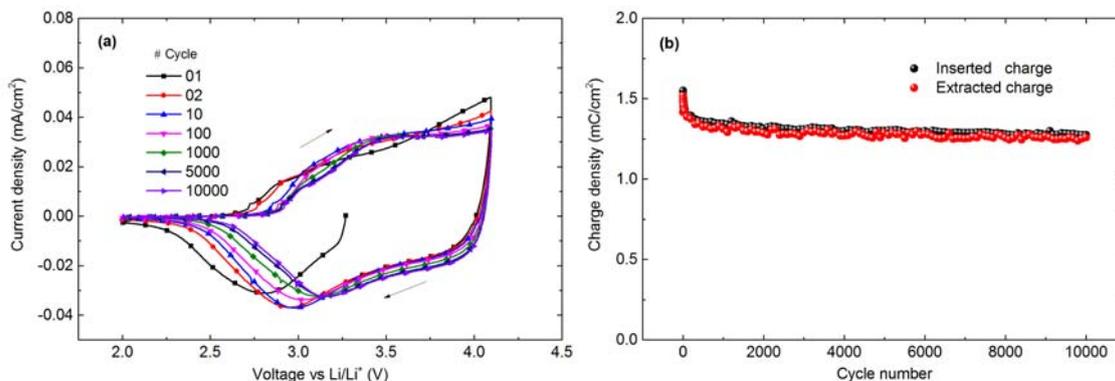


Figure 3. Electrochemical characteristics of the durability of Ni oxide thin films. Panel (a) shows cyclic voltammograms of films in 1 M Li-PC between 2.0 and 4.1 V vs Li/Li⁺; arrows signify voltage sweep direction. Panel (b) illustrates decay of charge density upon cycling.

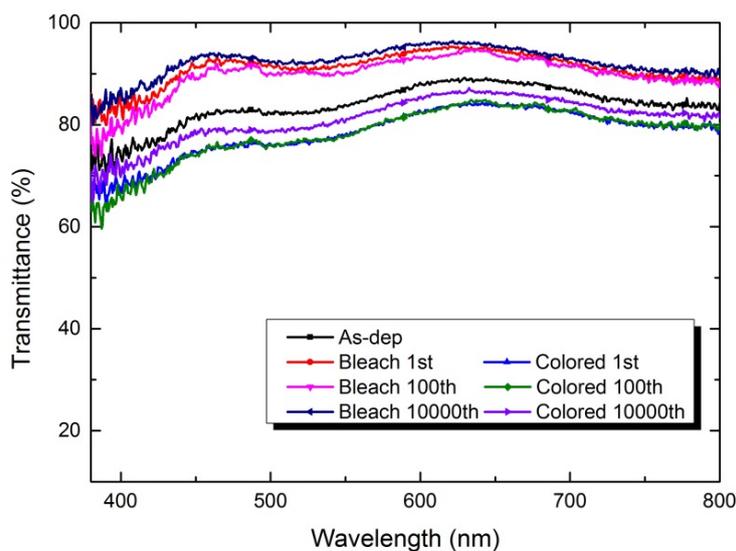


Figure 4. *In situ* optical transmittance of Ni oxide films in 1 M Li-PC before and after 100 and 10,000 cycles.

4. Conclusions

In summary, Ni oxide can be used as a stable EC layer in smart windows. XRD shows that the Ni oxide thin films still have a cubic structure after 10,000 electrochemical cycles in Li-PC. A rapid drop of charge density happens only during the first hundreds of cycles, and Ni oxide was found to be very stable upon further electrochemical cycling. A slight decrease of optical modulation was due to the small drop of charge density after long-term cycling.

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