



# Electrochromic nickel oxide films and their compatibility with potassium hydroxide and lithium perchlorate in propylene carbonate: Optical, electrochemical and stress-related properties



Rui-Tao Wen<sup>\*</sup>, Gunnar A. Niklasson, Claes G. Granqvist

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

## ARTICLE INFO

### Article history:

Received 21 February 2014

Received in revised form 30 June 2014

Accepted 2 July 2014

Available online 9 July 2014

### Keywords:

Nickel oxide

Thin film

Electrochromism

Stress

Transmittance

Durability

## ABSTRACT

Porous nickel oxide films were deposited onto unheated indium tin oxide coated glass substrates by reactive dc magnetron sputtering. These films had a cubic NiO structure. Electrochromic properties were evaluated in 1 M potassium hydroxide (KOH) and in 1 M lithium perchlorate in propylene carbonate (Li-PC). Large optical modulation was obtained for ~500-nm-thick films both in KOH and in Li-PC (~70% and ~50% at 550 nm, respectively). In KOH, tensile and compressive stresses, due to the expansion and contraction of the lattice, were found for films in their bleached and colored state, respectively. In Li-PC, compressive stress was seen both in colored and bleached films. Durability tests with voltage sweeps between  $-0.5$  and  $0.65$  V vs Ag/AgCl in KOH showed good durability for 10,000 cycles, whereas voltage sweeps between 2.0 and 4.7 V vs Li/Li<sup>+</sup> in Li-PC yielded significant degradation after 1000 cycles.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

The atmospheric content of carbon dioxide has risen from ~315 ppm in the late 1950s to ~400 ppm in 2013, and the increase rate has tripled—from ~0.7 to ~2.1 ppm per year—during the same period. The increased amount of CO<sub>2</sub> is largely an effect of fossil fuel burning and other human activities and is generally believed to have far reaching consequences with regard to human life, as recently reported by the Intergovernmental Panel on Climatic Change, under the auspices of the United Nations [1]. Drastic reductions in the use of fossil fuel, as well as a global transition to renewable energy sources, are needed to combat the effects of the growing CO<sub>2</sub> concentration. The building sector is of particular interest in this context since it accounts for 30 to 40% of today's use of primary energy globally [2]. This fraction tends to increase and, to take a specific example, the buildings' share of the primary energy consumption in the USA was 41% in 2010, whereas it was only 34% in 1980 [3].

Energy savings in buildings is a huge and largely untapped resource for CO<sub>2</sub> abatement [4]. Many “green” technologies—often with nano-structural attributes—can be implemented in buildings [5–7], and energy efficient fenestration is a particularly attractive option that can offer also improved indoor comfort [8] and financial benefits [9].

Windows are usually weak links in the buildings' energy systems and typically let in or out too much energy that needs to be compensated by cooling or heating. It is obvious that “smart windows”, with variable throughput of solar energy and visible light, can diminish the energy expenditure. Electrochromic (EC) “smart windows” have been under development for decades and are currently being implemented in buildings [10]. These windows normally include a multilayer structure with two different EC thin oxide films joined by an electrolyte, and this three-layer stack is surrounded by transparent electrical conductors [11]. Optical absorption is modulated when a voltage is applied between the electrodes and is associated with charge transfer between the EC films [11].

Electrochromism in tungsten oxide films has been known for about forty years; these films color under charge insertion (cathodically) [12]. In practical constructions, the W oxide films need to be complemented by films that ideally color under charge extraction (anodically). Iridium oxide films have this desired property, and devices based of W-oxide-based and Ir-oxide-based thin films have been cycled electrochemically for millions of times [11]. However Ir oxide is too expensive for large scale applications, even when diluted with less costly Ta oxide [13,14] or Sn oxide [15–17], and nickel-oxide-based alternatives have been studied since the mid-1980s [18–20]. Devices incorporating W-oxide-based and Ni-oxide-based films have attracted much interest [21], and EC “smart windows” using this combination of materials are currently introduced on the market [10]. However, the Ni-oxide-based films are still in need of refinement, and research on Ni-oxide-based films is

<sup>\*</sup> Corresponding author.

E-mail address: [Ruitao.Wen@angstrom.uu.se](mailto:Ruitao.Wen@angstrom.uu.se) (R.-T. Wen).

pursued vigorously; recent (2009 and later) studies have been published on such films prepared by evaporation [22], sputtering [23–27], chemical vapor deposition [28], various wet-chemical techniques such as sol–gel deposition [29–36] and chemical bath deposition [37–44], and electrodeposition [44–49]. Electrochromic Ni-oxide-based films have been made also by the electrophoretic deposition of Ni hydroxide nanoparticles [50] and from Ni oxide pigments deposited from water dispersion [51]. The electrochromism of binary Ni-based mixed oxides have attracted much attention during recent years, and results have been presented for such oxides containing Li [52–54], C [55,56], N [57], F [58], Al [59], Ti [60], V [61,62], Mn [49], Co [33], Cu [63], and W [25]. Ternary Ni-based oxides or nanocomposites containing Li–Al [64], Li–Zr [65], and Li–W [66] have given particularly interesting results. Finally we note that work has been reported also for number of hybrid materials of NiO–Q, where Q stands for poly(3,4-ethylenedioxythiophene) [67], polypyrrole [68], polyaniline [42], graphene oxide [69], and LiPON [70].

Generally speaking, the EC and other properties of Ni-oxide-based films can be improved by adding a second element, which explains the intense interest in them as noted above. The present paper lays a foundation for a comprehensive investigation of electrochromism in the Ni–Ir oxide system—with a scope that is similar to the one in our recent work on the electrochromism in the full Ni–W system [23,25, 71–73]—but is of interest also in its own right. Data on pure Ir oxide immersed in propionic acid, potassium hydroxide (KOH), and lithium perchlorate in propylene carbonate (Li–PC) were presented recently [74]. Below we investigate pure Ni oxide in KOH and Li–PC under experimental conditions that were carefully chosen in order to allow direct comparison with data on Ir oxide (propionic acid was not considered since Ni oxide is not stable in acids).

## 2. Experimental details

### 2.1. Thin film deposition

Thin films of nickel oxide were made by reactive dc magnetron sputtering in a coating system based on a Balzers UTT 400 unit. The substrates were  $5 \times 5 \text{ cm}^2$  glass plates with transparent and electrically conducting layers of  $\text{In}_2\text{O}_3\cdot\text{Sn}$  (known as ITO) having a sheet resistance of 60  $\Omega$ . No substrate heating was used. The target was a 5-cm-diameter plate of metallic nickel (99.95%), and the target–substrate separation was 13 cm. Pre-sputtering took place in argon (99.998%) for 5 min, and oxygen (99.998%) was then introduced. During deposition, the  $\text{O}_2/\text{Ar}$  gas-flow ratio was set at a constant value of 2.5%. The total pressure during sputtering was maintained at  $\sim 4$  Pa, and the power at the target was 200 W. Film uniformity was ensured by substrate rotation during the depositions. The film thickness  $d$  was determined by surface profilometry using a DektakXT instrument. Most films had a thickness  $d$  of  $\sim 500$  nm. Further experimental details are given elsewhere [75].

### 2.2. Structural and compositional characterization

Film structures were determined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer operating with  $\text{CuK}\alpha$  radiation at a wavelength  $\lambda_x = 0.154$  nm. The measurement took place at room temperature with a grazing incidence angle of  $1^\circ$  in parallel beam geometry with a  $2\theta$  ( $\theta$  was defined as the diffraction angle) between  $10^\circ$  and  $90^\circ$ . The step size was  $0.0200^\circ$ . Structure and phase composition were obtained by comparison with the Joint Committee on Powder Diffraction Standards (JCDPS) data base.

Linear grain sizes  $D$  were determined by the use of the Scherrer's formula [76], i.e.,

$$D = \frac{k\lambda_x}{\beta \cos\theta}, \quad (1)$$

where  $k \sim 0.9$  is a dimensionless “shape factor”,  $\beta$  is the full width at half-maximum of an X-ray diffraction peak, and  $\theta$  denotes the diffraction angle.

Morphology and porosity of the films were characterized by scanning electron microscopy (SEM) using a LEO 1550 FEG Gemini instrument with an acceleration voltage of 10 to 15 kV.

Elemental compositions and atomic concentrations were determined by Rutherford Backscattering Spectrometry (RBS) at the Uppsala Tandem Laboratory, specifically using 2 MeV  $^4\text{He}$  ions backscattered at an angle of  $170^\circ$ . The RBS data were fitted to a model of the film–substrate system by the use of the SIMNRA program [77].

Film density  $\rho$  was computed from

$$\rho = \frac{MN_s}{n_a N_A d}, \quad (2)$$

where  $M$  is the molar mass,  $N_s$  is the areal density of atoms,  $n_a$  is the number of atoms in a molecule, and  $N_A$  is the Avogadro's constant.

### 2.3. Electrochemical and optical measurements

Cyclic voltammetry (CV) was performed in a three-electrode electrochemical cell by the use of a computer-controlled ECO Chemie Autolab/GPES Interface. The Ni oxide film served as a working electrode and was electrochemically cycled in electrolytes consisting of 1 M KOH and 1 M Li–PC. For the KOH electrolyte, the counter electrode was a Pt foil and the reference electrode was Ag/AgCl; the voltage range was  $-0.5$  to  $0.65$  V vs Ag/AgCl. In the case of Li–PC, both counter and reference electrodes were Li foils, and the voltage range was 2.0 to 4.7 V vs Li/Li $^+$  which, importantly, was chosen to be the same as in our earlier investigation of Ir oxide films [74]. The voltage sweep rate was 10 mV/s, except for studies of long-term cycling durability when it was 50 mV/s.

Optical transmittance measurements were recorded in situ during electrochemical cycling of Ni-oxide-based 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 recorded before immersion of the sample in the electrolyte.

Electrochemical and optical measurements were employed to record the coloration efficiency (CE), which is defined as the difference in optical density per amount of charge exchange ( $\Delta Q$ ). Specific data were obtained from

$$\text{CE} = \frac{\log\left(\frac{T_{bl}}{T_{col}}\right)}{\Delta Q}, \quad (3)$$

where  $T_{bl}$  and  $T_{col}$  are the transmittance values for films in their fully bleached and colored states, respectively, and it is assumed that the related modulation in reflectance is small. It is desirable for most electrochromic devices, including “smart windows”, that the CE should be as large as possible.

## 3. Results and discussion

Fig. 1 shows SEM images of a typical  $\sim 500$ -nm-thick as-deposited Ni oxide film. Panels (a) and (b) show that the film has a distinct surface morphology with triangular features having linear extents of  $\sim 40$  nm or less. The cross-sectional image in Fig. 1(c) indicates a columnar nanostructure. This structure is as expected from the thin film deposition conditions—with a high pressure in the sputter plasma and a low substrate temperature—and is consistent with zone 1 in a “Thornton diagram” [78]. The columnar features are favorable for electrochromism [79].

Download English Version:

<https://daneshyari.com/en/article/1665308>

Download Persian Version:

<https://daneshyari.com/article/1665308>

[Daneshyari.com](https://daneshyari.com)