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Electrochromism in Ni Oxide Thin Films Made by Advanced Gas Deposition and Sputtering: A Comparative Study Demonstrating the Significance of Surface Effects

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Abstract

Films of electrochromic Ni oxide, with thickness in the ~100–1000-nm range, were prepared by reactive advanced gas deposition (AGD) and, for comparison, also by reactive DC magnetron sputtering (MS). Voltammetric cycling was performed in an electrolyte of lithium perchlorate in propylene carbonate in the voltage range 2.0–4.1 V vs. Li/Li⁺, and concurrent optical transmittance modulation was studied at a wavelength of 530 nm. For the thickest films, the optical modulation range was as large as ~54% and the maximum transmittance was ~82% for deposition by AGD, whereas the corresponding numbers were ~45% and ~87% for MS. Rutherford backscattering spectrometry together with measurements of film thickness demonstrated that the porosity of 400–500-nm-thick films made by AGD and MS were ~84% and ~45%, respectively. The charge exchange per mass unit was as high as 48–67 C g⁻¹ for samples made by AGD. The corresponding number was much lower for MS, namely 13–18 C g⁻¹. These results lend convincing support to the view that the electrochromism of Ni-oxide-based films in Li-ion-conducting electrolytes is dominated by surface effects.

Keywords: Electrochromism; Thin films; Nickel oxide, Thickness; Sputter deposition; Advanced gas deposition.

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Introduction

Electrochromic (EC) materials are characterized by their ability to sustain persistent and reversible changes of the optical properties upon the application of a voltage.^{1–3} A number of oxides exhibit pronounced electrochromism and are durable enough for applications such as variable-transmittance smart glazing (windows and glass facades).^{4–6} This kind of glazing is currently gaining popularity and is used in buildings that are energy efficient and have excellent indoor comfort.^{7–10} Other uses of oxide-based EC materials include variable-reflectance mirrors, non-emissive displays, and variable-thermal-emittance devices for temperature control. EC functionality can be combined with, *e.g.*, energy generation,¹¹ energy storage,^{12–16} and luminescence;¹⁷ furthermore, “dual-band” devices can display separately controlled EC properties in different wavelength intervals.^{18,19}

Most of today’s (2020) practically used EC smart glazing employs W-oxide-based and Ni-oxide-based thin films that are joined by an ion conductor being an inorganic thin film or a layer of a polymer electrolyte.^{4,20–23} This three-layer stack is surrounded by oxide-based transparent electrical conductors. Optical modulation occurs when a potential, of the order of a few volts, is applied between the transparent electrical conductors so that ion transport occurs between the W-oxide-based and Ni-oxide based films and a concurrent flow of charge balancing electrons takes place. The ion species in present-day smart glazing is H^+ or Li^+ , but other ions such as Al^{3+} may be useful too.^{24–27} The electrochromism of W-oxide-based materials is well known and is associated with reversible ion intercalation and polaron absorption,^{1,28,29} whereas modeling of the coloration mechanism in Ni-oxide-based materials is more challenging especially for Li-ion-conducting electrolytes. In this latter case, it has been clearly shown through recent work that surface effects play an important role and that not only cations but also anions can be important.^{30–35} We note, in particular, a prior investigation in which the EC properties of thin Ni oxide films, prepared by reactive DC magnetron sputtering (MS), were found to differ depending on whether (111) or (200) crystal facets of NiO were found predominantly at the external surface of the film.³² Nevertheless, some influence of Li-ion intercalation cannot be excluded.³⁶

Clearly there are a number of outstanding issues for EC Ni-oxide-based materials, and it is not surprising that thin films have been studied extensively during recent years. A wide variety of techniques have been used, and work since 2014 includes physical vapor deposition (pulsed laser deposition,³¹ evaporation,^{33,37} RF magnetron sputtering,^{38–47} and DC magnetron

sputtering^{22,23,32,34,36,47–67}), various chemical deposition techniques,^{12,30,31,68–94} and electrochemical deposition;^{75,80,95–101} work during 2007–2013 were surveyed in an earlier publication.⁴ A common feature of the mentioned techniques is that the nanostructure of the deposit is inextricably connected with the deposition process, as has been studied in detail especially for films produced by physical vapor deposition.^{102–105} This interdependency clearly is a serious limitation in work aimed at elucidating the specific role of surface effects on nanomaterials, as in the present case of EC Ni-oxide-based thin films. We therefore have chosen gas deposition¹⁰⁶ as the primary technique for making samples. This technique is noteworthy for its ability to separate the fabrication of individual nanoparticles from their subsequent deposition as a consolidated material on a substrate. Gas deposition is amenable to well-controlled thin-film manufacturing and is even industrially viable;^{107,108} the manufacturing technique is then commonly referred to as advanced gas deposition (AGD) and is described in some detail below. We are not aware of any prior work on EC Ni oxide made by AGD, but this technique has been used before to make EC W oxide films.¹⁰⁹ Furthermore, AGD has been used successfully to produce conductometric gas sensors based on Ni oxide^{110–112} and W oxide,^{113–121} whose performance is critically dependent on nanostructure; in addition, AGD has been employed recently for gas sensors based on surface-capped noble metal nanoparticles.^{122–125}

Experimental section

Film preparation.—Figure 1 is a schematic description of the unit for making highly porous films of Ni oxide by AGD (Ultra Fine Particle Equipment, ULVAC Ltd., Japan). In essence, the apparatus comprises two stainless-steel chambers connected by a pipe. The lower chamber, where an evaporation source is located and nanoparticles are produced, contains a gas which is let in continuously, while the upper chamber, where a particulate deposit is formed on a substrate, is evacuated by a vacuum pump. The upper part of the transfer pipe has a nozzle which determines the gas flow into the upper chamber and thereby the deposition rate for the nanoparticles.

The samples were produced by heating pellets of Ni (purity 99.9%) in a carbon crucible via an RF coil. The evaporated species were cooled and oxidized in a laminar flow of 20 L/min of He (purity 99.997%) and 0.1 L/min of O₂ (purity 99.998%). The Ni oxide nanoparticles formed in the gas were transported via the transfer pipe into the upper chamber where porous deposits were made onto glass substrates precoated with transparent and electrically conducting In₂O₃:Sn (ITO; 60 Ω/square) and simultaneously onto substrates of glassy carbon. The

substrates were mounted on a programmable X–Y-movable holder which enabled uniform deposits over areas of $4.0 \times 3.2 \text{ cm}^2$. Helium was chosen as the main gas since it can yield especially small particles.^{106,126} Specifically, our samples were prepared with pressures of 14–18 and 0.25–0.35 kPa in the lower and upper chamber, respectively, and a heating power of 3.5–4.3 kW. The substrate moved at a rate of 1.25 or 2.5 mm s⁻¹ and the beam of nanoparticles was swept two to four times over the substrate in order to make a deposit of appropriate thickness. Thin deposits were visibly brownish whereas thick ones were almost black. The particle size distribution obtained from AGD is known to exhibit a log-normal distribution,^{106,127,128} but this aspect was not elaborated on in the present study.

For comparison, we also prepared samples in a deposition system for reactive DC magnetron sputtering (UTT 400, Balzers AG, Liechtenstein). Films were deposited from a 5-cm-diameter target of Ni (purity 99.99%) onto substrates of the same kind as for AGD. The deposition unit was evacuated to $\sim 6 \times 10^{-5}$ Pa and pre-sputtering took place in Ar (purity 99.997%) for 5 min to remove target contamination. O₂ (purity 99.997%) was then introduced and its flow rate was adjusted to have an O₂/Ar ratio of 0.035 and a total gas pressure of 4 Pa. Sputtering onto unheated substrates was performed at a constant power of 200 W. The target–substrate separation was ~ 13 cm. Substrate rotation assured uniform deposits.

Techniques and procedures.—Film thickness d was measured *ex situ* by surface profilometry (Bruker Dektak XT) and by scanning electron microscopy (SEM; Zeiss LEO 1550, acceleration voltage 10 kV). The latter technique was used also to image the films' surfaces. Dividing d with deposition time gave thin-film deposition rates of 0.04–0.4 nm s⁻¹ and ~ 0.42 nm s⁻¹ for AGD and MS, respectively.

Elemental analyses were carried out by Rutherford backscattering spectrometry (RBS) using facilities at the Tandem Laboratory of Uppsala University. Specifically, the present work used 2 MeV ⁴He primary ions. Backscattered particles were detected at an angle of 170° with respect to the primary beam. Data were recorded for Ni oxide films backed by carbon substrates (instead of ITO) in order to avoid problems with features of In and Sn which, depending on thickness, would tend to obscure features due to Ni, and also to avoid overlap of oxygen signals from the film and the substrate. The RBS spectra were fitted to a model of the film–substrate system by use of the SIMNRA code.¹²⁹ This procedure allowed determinations of O/Ni atomic ratios as well as film density ρ by using the formula

$$\rho = \frac{MN_s}{n_a N_A d} , \quad (1)$$

where M is molar mass of NiO_x , N_s is areal density of atoms obtained from the RBS measurement, n_a is the number of atoms in a “ NiO_x molecule”, and N_A is Avogadro’s constant. Structural characterization was done by grazing incidence X-ray diffraction (XRD) using a Siemens D5000 instrument operating with Cu K_α radiation (wavelength 1.5418 Å).

Electrochemical measurements with cyclic voltammetry (CV) were performed by use of a potentiostat (Solartron 1286) together with a conventional three-electrode cell with Ni oxide thin films on ITO-coated glass serving as working electrodes, Li foil used as reference and counter electrodes, and an electrolyte of 1 M LiClO_4 (purity 98%) in propylene carbonate (PC, purity 99%). The CV measurements were made in the voltage range 2.0–4.1 V at a scan rate 50 mV s^{-1} . All voltages refer to Li/Li^+ . The inserted and extracted charge density during each cycle, Q , was obtained from the CV curves by integrating the negative and positive areas of the CV curves, respectively, according to

$$Q = \int \frac{j dV}{s} , \quad (2)$$

where j is current density, V is potential, and s is scan rate. The values for the negative and positive parts of consecutive voltage scans were reassuringly similar (some minor differences will be noted later, however).

The light source consisted of a fiber-coupled light-emitting diode (LED) controlled in constant-current mode by a LED driver (DC4100, Thorlabs). Optical transmittance, T , was recorded *in situ* at a wavelength of 530 nm (M530F2, Thorlabs). The 100-%-level for optical transmittance was the reading with nothing but electrolyte in the cell. All electrochemical and optical measurements were done in Ar atmosphere in a glove box with water content less than 2 ppm.

Measurements of Q and T enabled calculations of coloration efficiency, CE, by

$$\text{CE} = \frac{\ln(T_b/T_c)}{Q} , \quad (3)$$

where the subscripts b and c refer to the to fully bleached and colored states for the Ni oxide films, respectively.

Results and Discussion

Structure and composition.—Film thicknesses determined by surface profilometry were found to lie in the ranges 170–1020 and 130–1060 nm for samples made by AGD and MS, respectively. Table I states actual thicknesses recorded for six samples prepared by AGD (rows 1–6) and six samples made by MS (rows 7–12). Also, film thicknesses were determined by SEM cross-sections for all samples. Data obtained with the two techniques agreed to within $\pm 13\%$. The SEM data were obtained on as-deposited samples without any special preparation. Film thicknesses represent averages over five or six individual recordings. Figure 2 shows cross-sectional SEM images for two samples made by advanced gas deposition (AGD-4 and AGD-6) and two samples made by magnetron sputtering (MS-3 and MS-6). These samples were ~ 400 – 1000 nm thick and allowed us to perform analyses of characteristic nanostructures. The films made by AGD were comprised of 30 ± 10 -nm-diameter rounded structures, which are larger than the crystallite grain sizes (~ 12 nm), obtained from Scherrer analysis of XRD spectra. Therefore, we interpret the structures observed in the upper panels in Fig. 2 as NiO aggregates that appear uniform across the films' thicknesses. The films prepared by MS displayed somewhat tapered columns with axes normal to the substrate, which is a characteristic feature for deposits made by physical vapor deposition.^{102–105} The cross-sectional column diameter increased from 90 ± 30 nm for the 425-nm-thick film to 150 ± 30 nm for the 1060-nm-thick film. The two thinnest sputter deposited films displayed less well-developed columns that were difficult to analyze, but columnar features with diameters of ~ 50 nm, or even smaller, were indicated. In all cases, the column size is larger than the crystallite size of 10–12 nm obtained from XRD on films deposited under these and similar conditions.³²

In addition, SEM was used to show the morphology of the films' surfaces, as reported in Fig. 3 for AGD-prepared samples (upper set of six panels) and MS-prepared samples (lower set of six panels). The former samples were distinctly porous and characterized by nanoparticle aggregates that increased from ~ 50 to ~ 200 nm in linear size when the thickness was increased from 170 to 1020 nm. These features are probably related to the protrusions on the surface that can be seen in Fig. 2 (upper panels). Films made by MS, on the other hand, appeared more compact and showed nanofeatures that evolved from particulates with sizes of ~ 30 – 50 nm at a film thickness of 130 nm to regular triangular objects with a linear size of 100–150 nm at a film thickness of 1060 nm. This is apparent in Fig. 3 (lower panels). Triangular nanofeatures in Ni-oxide-based films made by sputtering have been reported also in earlier work.^{32,52}

Ni oxide films were studied by RBS in order to elucidate composition and porosity (denoted Φ). Figure 4 shows data for films on carbon substrates, specifically for one sample made by advanced gas deposition (AGD-4) and another sample made by magnetron sputtering (MS-3). Results on O/Ni ratios are included in Table I, where it is seen that this parameter is 1.65–2.33 for the three studied AGD-prepared films and 1.17–1.34 for the six MS-prepared films. The fact that this ratio is larger than unity may be due to the presence of hydroxyl groups and surface-adsorbed water molecules; the results for the sputter deposited samples were in agreement with those in earlier work.^{32,52} We note that the porous AGD-produced samples were exposed to environmental humidity, and hence surface-adsorbed water molecules are to be expected. The RBS data also showed evidence for substantial amounts of C and H in the films. Although these amounts were difficult to quantify, the data point to of the order of 10 at% C and 20 at% H in the sputter deposited films and to significantly higher quantities in the samples made by AGD. These findings are consistent with compounds formed at internal surfaces of the films provided that the surface-to-volume ratio would increase with increasing porosity. The fact that the O/Ni ratios were significantly larger for samples made by AGD than by MS may be associated with the higher hydrogen content and the much larger porosity of the former ones, as elaborated below.

The RBS data also allow evaluation of film density by use of Eq. 1. Results are given in Table I and show values as small as 0.39–1.07 g cm⁻³ for samples made by AGD. The fact that ρ was enhanced for increasing film thickness may suggest that consolidation of the deposit took place by the impact of impinging nanoparticles during longer deposition times. For samples made by MS, the density was 3.12–3.97 g cm⁻³. Film porosity was obtained by comparing the measured value of ρ with the density of bulk NiO (6.67 g cm⁻³), which gave the values shown in Table I. Clearly, the AGD-produced samples were very loosely packed with porosities as high as $84 \leq \Phi \leq 94\%$. The MS-produced samples had porosities of $41 \leq \Phi \leq 53\%$; these values are smaller than in prior work on sputter-deposited films.³²

XRD data verified the well-known cubic fcc structure of NiO. Figure S1 in Supporting Information reports data on sample AGD-6 and shows characteristic strong peaks of NiO with indices (111), (200) and (220) together with a weak (311) peak. These features agreed with International Center for Diffraction Data File ICCD-000471049. Analogous results for sputter-deposited Ni oxide films have been observed in previous work.^{32,130}

Charge exchange during voltammetric cycling, and electrochromism.—Figure 5 shows CV data for Ni oxide films made by AGD (upper set of six panels) and MS (lower set of six panels). Data refer to different film thicknesses and different numbers of cycles. The first CV cycle started at the open circuit potential and proceeded towards higher potentials. The shapes of the voltammograms, as well as their encircled areas (charge density Q , defined in Eq. 2), evolved during CV cycling; detailed results on Q vs. cycle number are given in Fig. S2 in Supporting Information. Data on Q vs. film thickness, recorded after 100 CV cycles, are shown in Fig. S3, which demonstrates that, expectedly, Q goes up in proportion with d . Looking again at Fig. 5, samples prepared by AGD displayed significant decline of charge density exchange upon CV cycling, which is especially evident for the thickest sample. Films made by MS, on the other hand, displayed only marginal drops of Q during the first 100 CV cycles. These latter results are consistent with data on similar samples in prior works^{49,52} which showed that Q vs. cycle number could be reconciled with by a power-law expression for at least as many as $\sim 10^4$ cycles.

Optical transmittance modulation during charge exchange—*i.e.*, electrochromism—is reported in Fig. 6 for all of the Ni oxide samples, and the data are organized in full analogy with those in Fig. 5. Figure 6 depicts optical modulation during 100 CV cycles during a time span of 8400 s. Corresponding voltammograms for a few selected cycle numbers were given in Fig. 5. Looking first at the data for AGD-produced samples (upper set of panels in Fig. 6), it is seen, expectedly, that the modulation range became progressively wider as the film thickness was increased. The transmittance varied between a high value of 94–98% (except for the thickest sample, AGD-6, where the upper limit was 81%) and a low value that was decreased as the thickness was increased. Some ageing is manifested as an increase of the lower limit of the transmittance during extended CV cycling. Considering samples made by MS (lower set of panels in Fig. 6), most features are the same as for the AGD-prepared films although a close examination of films with similar thicknesses shows that AGD yields somewhat higher optical modulation range and more pronounced degradation during extended cycling. The overall similarities of the electrochemical and optical data can be extended to the coloration efficiency (except, perhaps, for the very thinnest and thickest films), as evident from data in Fig. S4 in Supporting Information.

Significance of surface effects on electrochromism.—At face value, the data on current density and charge exchange in Fig. 5 and on optical modulation in Fig. 6 look more or less alike for samples with similar thicknesses though prepared by AGD and by MS. Thus, for

example, ~1000-nm-thick films made by AGD showed an optical modulation range of ~54% and a maximum transmittance of ~82% at the end of the voltammetric cycling, whereas the corresponding numbers for a film made by MS were ~45% and ~87%, respectively. However, this similarity, and others, is deceptive since the AGD-produced films have much higher porosity than the MS-produced films, *i.e.*, the former ones have a much smaller mass per area unit than the latter. We elucidate the issue of different porosities by showing density of inserted and extracted charge during cyclic voltammetry *per mass unit*, denoted Q_m . Specifically, we derive values of

$$Q_m = \frac{Q}{d\rho} \quad (4)$$

and show those in Fig. 7 for inserted as well as extracted charge.

The most salient result of Fig. 7 is that charge exchange per mass is much larger in samples made by AGD than by MS. Specifically, this parameter is 48–67 C g⁻¹ for AGD but only 13–18 C g⁻¹ for MS, *i.e.*, there is a difference corresponding to a factor three to four. Results for charge insertion and charge extraction do not differ to any significant degree. The mere observation that Q_m is larger for the AGD films, which has about twice as high porosity as the MS films, unambiguously proves that the charge insertion/extraction cannot be a bulk process.

To further quantify the charge exchange, it is useful to compare the ratio of the amount of inserted charge to the number of “NiO_x molecules”, z , for the two types of samples. This ratio is obtained from

$$z = \frac{Q_m M}{e N_A} \quad (5)$$

where e is the electron charge. These values are ~0.04–0.06 for samples prepared by AGD but only ~0.01–0.015 for samples made by MS. It is thus seen that a substantially larger portion of “NiO_x” is accessible for charge exchange in samples prepared by AGD. However, the values of z are still low, which strongly suggests that electrochromism in Ni oxide films, when operated in a Li-containing electrolyte, is to large extent a surface phenomenon.

The assertion above is supported by the SEM data, which showed that the AGD-prepared samples consisted of rounded aggregates, while the MS-prepared samples comprised densely packed columnar structures (*cf.* Fig. 2). We now assume that the electrolyte only accesses the surfaces of these aggregated structures and that charge exchange occurs into and out at the aggregate surfaces. The aggregate sizes of the AGD-prepared samples, inferred from Fig. 2

(upper panels), have dimensions of the order of 30 nm, which implies a surface-to-volume ratio, S/V , of 0.2 nm^{-1} assuming spherical geometry. The columnar structures in the films made by MS, on the other hand, were up to $\sim 1000 \text{ nm}$ long and, assuming cylindrical geometry and effective radii of $\sim 50\text{--}75 \text{ nm}$, we find that S/V is in the $0.025\text{--}0.04\text{-nm}^{-1}$ range. These numbers are consistent with the values of z given above, as we show below.

We can make an order-of-magnitude estimate of z by noting that

$$z = tS/V, \quad (6)$$

where t is the width of the surface layer accessible to the Li ions. Assuming $t = 0.4 \text{ nm}$, which is close to the lattice constant of NiO, and using the values of S/V stated above, we find for the samples made by MS that z is $\sim 0.01\text{--}0.016$, while the samples prepared by AGD yield $z \approx 0.08$. Modelling structural features as spheres for films made by AGD and cylinders for films made by MS are of course over-simplified representations of the true structures. Nevertheless, the correspondence between estimated and measured values of z suggests that our simple model captures essential features of the films' microstructures. Hence, the combined analysis of the inserted charge and morphology of the films gives strong evidence that the differences in Q_m and z between samples made by AGD and MS are due to surface-related effects.

Conclusion

We have compared the electrochromic properties of thin films of Ni oxide prepared by advanced gas deposition and by magnetron sputtering. The films deposited by AGD exhibited porosities of the order of 90%, which is much higher than for the films made by MS. Furthermore, the sizes of the aggregates in films made by AGD were $\sim 30 \text{ nm}$, while the films deposited by MS showed columns with diameters of $\sim 50\text{--}150 \text{ nm}$. These structural differences led to strikingly different electrochromic properties. Exchanged charge density and transmittance modulation increased approximately in proportion to thickness in a similar way for the two types of films despite the fact that the AGD-prepared films were more porous. A good indicator for comparing the electrochromic properties is the charge exchanged per unit mass, which is a factor of almost four higher for the films made by AGD. A larger portion of the Ni oxide is accessible to charge insertion and extraction in more porous films. However, the charge exchanged per "NiO" unit was low, even for the samples deposited by AGD, which

demonstrates that the electrochromism of Ni oxide in Li-containing electrolytes is, to a large extent, a surface phenomenon.

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Table I. Sample data for thin films of Ni oxide prepared by reactive advanced gas deposition (AGD) and reactive DC magnetron sputtering (MS).

Sample designation	Film thickness (nm)	O/Ni ratio	Density (g cm ⁻³)	Porosity (%)
AGD-1	170	2.33	0.39	94
AGD-2	190	1.95	0.49	93
AGD-3	380	—	—	—
AGD-4	475	1.65	1.07	84
AGD-5	500	—	—	—
AGD-6	1020	—	—	—
MS-1	130	1.34	3.12	53
MS-2	295	1.27	3.67	45
MS-3	425	1.27	3.64	45
MS-4	545	1.25	3.97	41
MS-5	640	1.17	3.80	43
MS-6	1060	1.30	3.46	48

Figure 1. Schematic rendition of the AGD unit for making highly porous films of Ni oxide. Adapted from Welearegay *et al.* (Ref. 125).

Figure 2. Cross-sectional scanning electron microscopy images of Ni oxide films prepared by reactive advanced gas deposition (AGD, upper panels) and reactive DC magnetron sputtering (MS, lower panels). Sample designations and film thicknesses are stated. Some debris from fractured glass substrates are visible. The scale bars are 500 nm.

Figure 3. Top-view scanning electron microscopy images of Ni oxide films prepared by reactive advanced gas deposition (AGD, upper set of six panels) and reactive DC magnetron sputtering (MS, lower set of six panels). Sample designations and film thicknesses are stated. The scale bars are 200 nm.

Figure 4. Rutherford backscattering spectrometry data of Ni oxide films prepared by reactive advanced gas deposition (AGD, upper panel) and reactive DC magnetron sputtering (MS, lower panel). Experimental results are shown along with simulations by SIMNRA accounting for the shown species. The composition in atomic percent obtained from the shown fits were 33% O, 20% Ni, 17 % C and 30% H for AGD-4 and 36% O, 29% Ni, 11% C and 23% H for MS-3. The hydrogen contents are very uncertain. Sample designations and film thicknesses are stated.

Advanced gas deposition

Figure 5. Cyclic voltammograms of Ni oxide films for different film thicknesses ranging from 170 to 1020 nm for AGD and from 130 to 1060 nm for MS, respectively. The samples were prepared by reactive advanced gas deposition (AGD, upper set of six panels) and reactive DC magnetron sputtering (MS, lower set of six panels) immersed in electrolytes of LiClO₄-PC. Data were taken after the indicated numbers of cycles. Sample designations and film thicknesses are stated. Arrows denote voltammetric scan direction. The CV measurements were made in the voltage range 2.0–4.1 V vs. Li/Li⁺ at a scan rate of 50 mV s⁻¹.

Advanced gas deposition

Figure 6. Optical transmittance at a wavelength of 530 nm *vs.* time of Ni oxide films for different film thicknesses ranging from 170 to 1020 nm for AGD and from 130 to 1060 nm for MS, respectively. The samples were prepared by reactive advanced gas deposition (AGD, upper set of six panels) and reactive DC magnetron sputtering (MS, lower set of six panels). Data were recorded during voltammetric cycling in electrolytes of LiClO₄-PC in the 2.0–4.1 V *vs.* Li/Li⁺ range at 50 mV s⁻¹. Time-resolved transmittance data are shown in insets for the thinnest films. The small bump seen for AGD-2 at 3000–4000 s appears to be an instrumental artefact.

Figure 7. Density of inserted and extracted charge normalized per mass unit, Q_m , vs. film thickness for Ni oxide films prepared by reactive advanced gas deposition (AGD) and reactive DC magnetron sputtering (MS). Data are for the 100th voltammetric cycle. Individual data points are joined by straight lines for clarity.

Supporting Information

Electrochromism in Ni Oxide Thin Films Made by Advanced Gas Deposition and Sputtering: A Comparative Study Demonstrating the Significance of Surface Effects

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Figure S1. XRD pattern of an as-prepared Ni oxide film deposited by AGD (sample AGD-6). The peaks are assigned to the shown atomic planes. Diffraction angle is denoted θ and the vertical scale represents arbitrary units (a.u.).

Figure S2. Charge density vs. cycle number for Ni oxide films prepared by advanced gas deposition (upper panel) and reactive DC magnetron sputtering (lower panel) immersed in electrolytes of LiClO₄-PC. Data were taken for films of the shown thicknesses and refer to inserted charge (dotted curves) and extracted charge (solid curves).

Figure S3. Charge density, Q , vs. thickness for Ni oxide films prepared by advanced gas deposition (upper panel) and reactive DC magnetron sputtering (lower panel) immersed in electrolytes of LiClO_4 -PC. Data were taken after 100 voltammetric cycles and refer to inserted and extracted charge.

Figure S4. Coloration efficiency vs. thickness for Ni oxide films prepared by advanced gas deposition (upper panel) and reactive DC magnetron sputtering (lower panel) immersed in electrolytes of LiClO₄-PC. Data were taken after 100 voltammetric cycles.