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Anodic Electrochromic Nickel Oxide Thin Films: Decay of Charge Density upon Extensive Electrochemical Cycling

Rui-Tao Wen,* Claes G. Granqvist and Gunnar A. Niklasson

R.-T. Wen, Prof. C.G. Granqvist, Prof. G.A. Niklasson
Department of Engineering Sciences, The Ångström Laboratory, Uppsala University
P. O. Box 534, SE-75121 Uppsala, Sweden
E-mail: Ruitao.Wen@angstrom.uu.se

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Abstract: Electrochromic (EC) Ni oxide thin film is a critical component in the “smart windows”. However, long-term decay of the EC performance in aprotic electrolytes is persistent and poorly understood, and it is difficult to assess life-times of EC devices. Here we report on charge density decline upon electrochemical cycling. The charge density decay was modeled with a *power law* or, alternatively, a *stretched exponential*; both models describe a rapid drop of charge density during the first hundreds of cycles and a subsequent slower decline. The decay is independent of film composition and applied potential range as long as the upper limit of the potential is ≤ 4.4 V vs. Li/Li⁺. Our decay models are interpreted in terms of dispersive chemical reaction kinetics and point at ion diffusion as the rate-limiting step. Power-law exponents are consistent with diffusion. The results provide a framework for evaluating EC durability of Ni-oxide-based thin films and may be important for assessing the durability of EC devices.

1. Introduction

Charge density degradation during extended electrochemical cycling is a ubiquitous phenomenon of much importance for energy-related applications and is responsible for charge/discharge decline in electrical batteries and loss of coloration/bleaching in electrochromic (EC) devices. Metal-oxide-based EC “smart windows”,^[1-4] for example, must be able to operate for decades^[5] in order to unleash their potential to provide energy efficiency combined with a comfortable indoor environment. Most EC windows for practical applications use a cathodically coloring W oxide thin film separated from an anodically coloring Ni oxide thin film by an electrolyte in thin-film form or being a polymer layer, and this three-layer configuration is embedded between transparent and electrically conducting thin films serving as electrodes.^[2,6-8] Optical modulation occurs when ions—typically protons or Li^+ —and charge-balancing electrons are shuttled between the EC films under the action of a voltage applied to the electrodes.

Crystalline NiO has a rock salt structure with one Ni atom and one O atom in a cubic unit cell. The valence band consists of almost completely hybridized Ni $3d$ and O $2p$ states, and the conduction band comprises unoccupied Ni $3d$ states with an admixture of O $2p$ states.^[9] NiO is a p -type semiconductor with cationic vacancies connected with the formation of Ni^{3+} .^[10] EC coloration and bleaching in Ni-oxide-based films occurs by extraction and insertion of $3d$ electrons in the valence band without affecting the metal–oxygen bond,^[6,7] and it is widely accepted that the optical absorption in the colored state is related to charge transfer between Ni^{2+} and Ni^{3+} sites. Most studies of EC Ni oxide thin films have dealt with aqueous electrolytes, especially potassium hydroxide (KOH),^[2] in which case the electrochromism is dominated by proton insertion/extraction^[11,12] and can be reconciled with the well-known Bode reaction scheme.^[13,14] However the electrochromism of Ni oxide in aprotic electrolytes, which is of interest in our present work, is different and is related to

adsorption of cations and anions on grain surfaces,^[15] accompanied by charge-balancing insertion/extraction of electrons in the valence band. Bleaching is then achieved by desorption of anions from Ni surface sites and/or adsorption of cations (Li^+) on $\text{O}_{\text{surface}}$ atoms at Ni oxide grain surfaces^[16] with concurrent injection of electrons into the Ni oxide film through the external circuit to compensate for charge imbalance; importantly, the inserted electrons are filling the Ni 3d valence band thereby yielding high optical transmittance. Coloration takes place by cation desorption^[16] from $\text{O}_{\text{surface}}$ atoms and anion adsorption on $\text{Ni}_{\text{surface}}$ atoms on Ni oxide grain surfaces,^[17] and electrons are extracted from the valence band so that the optical absorption is increased. The critical importance of the preferred orientations of the exposed crystallite surfaces for the achievable degree of coloration should be emphasized.^[15] Clearly, optical modulation can be accomplished by repeated charge exchange, and the optical properties remain constant in the absence of electrochemical side reactions at the film/electrolyte interface and without considering mechanical fatigue and failure. However, these conditions cannot be precisely fulfilled during absorption/desorption of anions/cations upon long-term cycling, and the effective life-time of EC Ni oxide films is then expected to be impaired. There are several previous studies on long-term durability of Ni-oxide-based thin films in non-aqueous electrolytes,^[18-21] but the degradation of charge density and optical modulation nevertheless remains poorly understood, and elucidating the mechanisms that govern charge density declination presents challenges for both theory and experiment. In addition, the role of film composition and applied potential needs to be explored in detail with regard to durability.

Here we present results from a comprehensive investigation of the effect of composition and applied potential range on charge density declination upon electrochemical cycling of sputter deposited Ni oxide thin films in a Li^+ -conducting electrolyte. The dynamics of charge density degradation is described in terms of *power-law* and *stretched-exponential* decay and is

influenced by the Ni^{3+} concentration. The underlying causes of these functions are explored within the framework of dispersive chemical reaction kinetics,^[22-26] which allows us to discuss microscopic mechanisms for the charge density evolution. Degradation of optical modulation is due to increased optical transmittance in both bleached and colored states, thus indicating a critical depletion of Ni^{3+} sites. Developing quantitative models of the degradation behavior will enable us to carry out life-time assessments for EC thin films as well as, in a later stage, perhaps also for complete EC devices. The present work is a sequel to an earlier study of ours^[15] showing that charge insertion/extraction in Ni oxide films immersed in aprotic electrolytes is a surface process, and it goes far beyond the preliminary discussion of degradation kinetics in an earlier Letter.^[21]

2. Experimental results

Ni oxide films were prepared by reactive DC magnetron sputtering onto glass plates pre-coated with transparent and electrically conducting $\text{In}_2\text{O}_3\text{:Sn}$ (ITO). Film composition was controlled by monitoring the oxygen content in the chamber during the deposition process. Film thicknesses were 290 ± 10 nm. Cyclic voltammetry (CV) was used for repeated charge exchange from an electrolyte of 1M LiClO_4 in propylene carbonate ($\text{LiClO}_4\text{-PC}$). The scan rate was 50 mV s^{-1} , the maximum number of CV cycles was 2000, and potentials were recorded with regard to Li/Li^+ . We were able to adjust the applied potential range and to record the amount of charge insertion/extraction in every CV cycle. X-ray diffraction measurements showed that all films had the face-centered cubic structure,^[15] as expected for NiO. Rutherford Backscattering Spectroscopy was used to ascertain elemental compositions, specifically being $\text{NiO}_{1.16}$, $\text{NiO}_{1.25}$ and $\text{NiO}_{1.32}$. Optical transmittance was recorded in the 380–800-nm range encompassing visible light. Further technical details can be found in the section

on Experiments and Methods and in our earlier article.^[15] As-deposited films looked darker the higher the oxygen concentration during sputter deposition, which suggests that their concentration of Ni^{3+} was higher; this concentration is important for the EC performance in $\text{LiClO}_4\text{-PC}$, as presented later.

2.1 Optical and electrochemical properties

Figure 1 illustrates how the optical properties are altered as charge is inserted and extracted in a $\text{NiO}_{1.16}$ film. CV was performed between a lower limit of 2.0 V and an upper limit set at a value U_H in the range 3.7 to 4.7 V. The films were bleached to almost the same transparent state, as high as ~90%, at the lower potential, and they were colored to an increasing degree as U_H was enhanced. We infer that the Ni 3d band is almost filled for the bleached film and is gradually emptied as U_H is enlarged, *i.e.*, as the Fermi level is lowered. Data for films of $\text{NiO}_{1.25}$ and $\text{NiO}_{1.32}$ ^[15] can be interpreted analogously.

Figure 2 presents cyclic voltammograms and spectral optical transmittance for films of $\text{NiO}_{1.16}$, $\text{NiO}_{1.25}$, and $\text{NiO}_{1.32}$ upon cycling between 2.0 and 4.1 V for up to 2000 cycles, and complementary electrochemical data for the 2.0–4.4 and 2.0–4.7 V ranges are given in Figure 3. The voltammograms in Figure 2 are similar except for the initial cycles in the case of $\text{NiO}_{1.32}$ where the bleaching process persists to a potential as low as 2.0 V, which is far below the potentials where bleaching is essentially complete for the other samples. Analogous changes are seen in Figure 3 for the voltage interval 2.0–4.4 V, whereas more pervasive changes are found for the interval 2.0–4.7 V. These observations may point at changes in the band structure for the film with the highest oxygen content, but we are unable to give any detailed explanation; initial cation adsorption may also be significant.^[15] The optical modulation, apparent in Figure 2, decays significantly during CV cycling, and both the

bleached and colored states become more transparent than after the second cycle. Hence the amount of Ni^{3+} sites decreases during electrochemical cycling, and this effect is larger for films with higher oxygen content and hence more initial Ni^{3+} sites. In the case of the $\text{NiO}_{1.32}$ film having undergone 2000 CV cycles, the colored-state transmittance is larger than in the as-deposited film. It can also be observed that the $\text{NiO}_{1.32}$ film displays the greatest optical modulation in the beginning of the cycling, and that the modulation falls off to approximately same level as for films of $\text{NiO}_{1.16}$ and $\text{NiO}_{1.25}$ after 2000 CV cycles (Figure 2a'–2c').

2.2. Degradation kinetics

Figure 4 shows charge density Q per CV cycle for coloration at varying values of U_H on a logarithmic (*log–log*) scale, and Figure 5 gives corresponding data on a linear (*lin–lin*) scale and indicates that the charge densities for coloration and bleaching are similar though not identical, and that the difference is largest for the highest potential range. The difference of the charge density for coloration and bleaching, denoted δQ , is shown in Figure 6. Clearly this parameter remains small for the narrower voltage intervals but becomes large for $U_H = 4.7$ V especially for the film of $\text{NiO}_{1.32}$. Somewhat enhanced values of δQ are noted also for $U_H = 4.4$ in the case of films of $\text{NiO}_{1.25}$ and $\text{NiO}_{1.32}$.

The data in Figure 5 display a characteristic rapid initial drop followed by a very slow decay of Q as the cycle number x progresses, regardless of film composition and potential range as long as $U_H \leq 4.4$ V. The gradual decline is highlighted when illustrated on a logarithmic scale, and Figure 4 indicates that this feature can be approximated, at least in certain ranges, by straight lines.

Numerous functional dependencies were tried in order to fit the data, and it was discovered that a *power-law* or, alternatively, a *stretched-exponential* expression could

describe the decline of the power density accurately, as apparent from Figure 4. Specifically, the fittings used the expressions

$$Q_1 = B_1 + \frac{A-B_1}{1+(\frac{x-1}{x_{01}})^{p_1}} \quad (1)$$

for the *power law* and

$$Q_2 = (A - B_2)e^{-D(x-1)^{p_2}} + B_2 \quad (2)$$

for the *stretched exponential*, where A is the initial charge density, *i.e.*, the charge density for the first CV cycle, and B_1 and B_2 are the residual charge density after long-term cycling. Furthermore, x_{01} and x_{02} are the cycle numbers at which the decline in Q has reached half of its final value, $D = \ln 2/x_{02}^{p_2}$ and, most significantly, p_1 and p_2 are exponents. Table I lists the actual fitting parameters.

The two equations lead to fits that are indistinguishable when one considers experimental uncertainties. The fitting parameters depend on film composition and potential window, and it is seen that the *power-law* exponent p_1 is larger than the *stretched-exponential* counterpart p_2 , as indicated in Figure 7. Furthermore $B_1 < B_2$ (with one exception) and $x_{01} > x_{02}$. Several trends can be noted among the data. *First*, all films, irrespective of composition, show excellent agreement with the degradation models encapsulated in Equations (1) and (2) when the applied potential is equal to or less than 4.4 V (top three rows in Figure 4). There is a slight deviation of charge density from the fit in the potential window 2.0–4.4 V at the approach of 2000 cycles, which signals the onset of a new degradation mechanism. This new process becomes much more significant when $U_H = 4.7$ V, as discussed in more detail shortly. *Second*, for a given composition it is found that larger potential windows lead to greater charge density, which is consistent with data in Figures 4 and 5. *Third*, films with large oxygen content showed a higher charge density at the beginning of the CV cycling, combined

with a greater drop upon continued cycling, than films with low oxygen content within the same potential window (Figures 4 and 5). *Fourth*, the values of the exponents p_1 and p_2 are largest for the smallest potential window and tend to drop as the oxygen content in the films is increased (Figure 7). *Fifth*, when U_H was set to 4.7 V, the charge density dropped rapidly at the beginning of the CV cycling, which is similar to the performance for the other potential windows and can be modeled with *power-law* or *stretched-exponential* degradation. However, further cycling leads to a slight increase in the charge density during a few hundred cycles, and then the charge density drops precipitously to zero (Figures 4 and 5). The latter phenomenon is caused by a disintegration of the film due to excessive ion absorption/desorption, as discussed next.

Figure 8 correlates the degree of degradation to the microstructure of the surface of the $\text{NiO}_{1.32}$ film, as observed by Scanning Electron Microscopy (SEM). For cycling at 2.0–4.4 V, the charge density exhibits an initial fast decay state (I) followed by a relatively steady state behavior (II) (Figure 8a). SEM revealed that the morphology was barely altered after 2000 CV cycles (Figures 8c and 8d). However, the SEM images looked very different when the potential range was expanded to 2.0–4.7 V, and Figure 8b shows that the charge density declination displays a fast decay state (I), an intermediate state (II), and a degradation state (III). Stage (I) is akin to the behavior for 2.0–4.4 V, but it is evident that $U_H = 4.7$ V leads to deterioration of the film's structure, and the adhesion between Ni oxide grains and between film and substrate becomes weak. Once this happens, the film structure gets more porous and expanded (Figure 8e). This open structure may be beneficial for ion absorption and desorption and is the likely cause of the increased charge density in the intermediate stage (II). However, the weak mechanical adhesion makes the film peel off from the substrate (Figure 8f), and this is accompanied by a sharp drop of charge density in stage (III); eventually nothing but the bare ITO surface is to be seen (Figure 8g). We observed small flakes of the films on the

bottom of the electrochemical cell after completion of the measurement. CV data in Figure 3 gives complementary information and provides supporting evidence of film degradation for the ranges 2.0–4.4 V and 2.0–4.7 V.

3. Discussion

We now discuss how to interpret the decay of charge density upon electrochemical cycling of Ni oxide films. So far our analysis was strictly empirical and amounted to nothing more than fitting of our experimental data to Eqs. (1) and (2), but we show below that these equations have physical and chemical significance. We first note that the degradation of the charge density exchange in EC Ni oxide thin films appears to be associated with a slight imbalance between charge densities for coloration and bleaching in each CV cycle (Figures 5 and 6). We previously argued^[15] that the coloration was due to adsorption of negative ions and desorption of positive (Li^+) ions from the surface during the positive potential sweep and that the opposite would hold for bleaching. As indicated in Figure 5, the coloration charge is larger than the bleaching charge (except for a few initial CV cycles in some cases), and hence it appears that the charge irreversibility is due to a fraction of the negative ions forming strong bonds with $\text{Ni}_{\text{surface}}$ sites so that these ions cannot desorb during the negative potential sweep. Obviously, this is a minor effect in each CV scan, but the imbalance evolves over many cycles, becomes large and leads to decay of the charge exchange. The irreversibly adsorbed species block part of the surface from taking part in the EC process, and therefore both inserted and extracted charge decays as a function of cycle number.

Reversible EC coloration/bleaching of Ni oxide can be modeled as an adsorption/desorption (ads/des) process wherein the adsorbate A binds weakly at the interface to the solid film S^[27] according to the schematic reaction

The adsorption process is commonly modeled by Langmuir adsorption theory^[27] so that the concentration C of adsorbed species in quasi-equilibrium is given by

$$C_{A^*S} = \frac{K_a C_A C_{tot}}{1 + K_a C_A}, \quad (4)$$

where K_a is the equilibrium constant and C_{tot} is the total concentration of surface sites. However, some of the negative ions must be bound more strongly to the surface and probably form a covalently bonded compound with the surface atoms. In the case of negative ions from our electrolyte reacting on the Ni oxide surface, a possible candidate would be the formation of nickel perchlorate, $Ni(ClO_4)_2$. Hence we must combine the adsorption process described above with an ensuing reaction step. There are two possibilities for such a reaction step: *First*, a second ion may diffuse from the electrolyte and react at an A^*S site so that

The reaction rate becomes^[24]

$$-\frac{dC_A}{dt} = \frac{K_2 K_a C_A^2 C_{tot}}{1 + K_a C_A}, \quad (6)$$

and it is observed that the reaction is of second order for low concentrations of A and of first order for high concentrations of A . A *second* possibility is that two adsorbed species diffuse on the film–electrolyte interface and form the compound A_2S once they meet each other, *i.e.*,

A simplified rate expression can be written as^[27]

$$-\frac{dC_A}{dt} = \frac{K_1 K_a^2 C_A^2 C_{tot}}{(1 + K_a C_A)^2}, \quad (8)$$

so that the reaction is of second order for low concentrations. The two possibilities described above are similar to the Eley–Riedel and Langmuir–Hinshelwood reaction schemes used in the field of heterogeneous catalysis.^[27] Clearly there are several possibilities, and it is even difficult to motivate from general considerations what would be the most probable reaction order.

Next we discuss how the above reaction schemes can give rise to the degradation kinetics observed in this study, *i.e.*, those given by the *power-law* and *stretched-exponential* expressions in Eqs. (1) and (2), respectively. These expressions arise naturally in the case of so-called dispersive chemical kinetics, as discussed in several comprehensive review papers by Plonka.^[22–26] Dispersive kinetics occurs when the rate constants K_1 and K_2 are time-dependent and given by *power-law* functions, *i.e.*,

$$K_i = Et^{\alpha-1} , \quad (9)$$

where α is the power-law exponent and E is a constant. Such *power-law* dependencies frequently appear when the reaction is diffusion limited, for example when the diffusion of reactants is modeled by a random walk.^[23,24] Integration of the first-order kinetic equation

$$-\frac{dC}{dt} = k(t)C, \quad (10)$$

gives directly a stretched-exponential expression similar to Eq. (1) by^[22]

$$c_A(t) = c_A(0)\exp\left(-\left(\frac{t}{\tau}\right)^\alpha\right), \quad (11)$$

where τ is a constant. A second-order rate equation

$$-\frac{dC}{dt} = k(t)C^2, \quad (12)$$

on the other hand, leads to power-law kinetics according to the expression^[22]

$$c_A(t) = \frac{c_A(0)}{\left(1 + \left(\frac{t}{\tau}\right)^\alpha\right)}, \quad (13)$$

which is similar to Eq. (2). In our model, the decrease of the charge density upon CV cycling is due to the lowering of the concentration of reversible adsorption sites A*S and is associated with the irreversible reactions described by either of the two schemes (5) and (7) outlined above. In the case of reaction (5), each reaction “consumes” one surface site and the decrease in concentration of A*S should be proportional to that of A. Reaction (7) is more complex, but the net result is expected to be the same there too.

As discussed above, the reaction order of the irreversible reaction on the Ni oxide surface may be either one or two depending on the specifics of the mechanism and on whether the concentration of the adsorbent is low or high. Furthermore, it is not possible to experimentally distinguish between the two expressions in Eqs. (1) and (2). However, it is noteworthy that many of the exponents p_1 and p_2 in Table I are clustered in the 0.4–0.6 range. The values of the exponents are not far from 0.5 (Figure 7) which corresponds to semi-infinite diffusion. This fact may lend some support to reaction scheme (5), which would then be limited by ion diffusion in the electrolyte towards the Ni oxide surface. Clearly, more detailed studies are necessary in order to fully explain the degradation mechanisms in EC Ni oxide thin films, and the use of electrolytes with different ion conductivities may be elucidating.

Charge density exchange directly determines the optical modulation of Ni oxide films since it represents the amount of charge-compensating electrons that are inserted or extracted in one CV cycle and alter the position of the Fermi level in the valence band. We found above that the decay of charge density leads to higher transparency for both bleached and colored states. Hence the charge decay must be associated with a decrease of the number of Ni^{3+} sites and an increase of the Ni^{2+} sites. This has two important consequences: *Firstly*, the irreversible schematic reactions represented by Eqs. (5) and (7) must be applicable also to

Ni³⁺ sites present in the as-deposited films. *Secondly*, the compound formed after these reactions must be divalent with respect to Ni.

It is clearly possible to use the *power-law* as well as the *stretched-exponential* model to estimate and predict how the charge density will evolve as the Ni oxide film is electrochemically cycled and how the concurrent optical modulation will unfold. Preliminary results of ours indicate that charge density decay in WO₃ follows similar models, and it should therefore be possible to use simple empirical expressions to estimate the practical life-time of EC devices. However, other degradation modes can appear for severely degraded EC films, as seen in the present work when CV cycling took place in the large potential range of 2.0–4.7 V. In the present case, 4.4 V may be considered a critical potential for Ni oxide above which severe degradation and failure sets in. We also note that galvanostatic materials rejuvenation is an option for extending the life-time at least for the case of WO₃.^[28-30]

4. Conclusions

We reported the decay of charge density exchange and associated optical modulation for sputter deposited Ni oxide thin films with different O/Ni ratios, and hence with different degrees of the preferred orientation of the crystallites comprising the film,^[15] upon electrochemical cycling in 1M LiClO₄–PC. A rapid drop of charge density exchange during the first few hundreds of cycles was followed by a slow decay, independently of film compositions and potential window. The degradation of the charge density could be reconciled with *power-law* as well as *stretched-exponential* models which, in their turn, may be related to dispersive chemical kinetics and involve a variety of diffusion-limited reactions that take place upon electrochemical cycling. Hence our parameterizations, irrespectively of degradation model and its underlying physics and chemistry, account for the decline of the

electrochromic performance. This result is significant since it offers a way to evaluate the life-time for Ni oxide films undergoing electrochemical cycling, and it may be of relevance also to other metal oxides as well as to electrochromic devices.

5. Experiments and methods

Ni oxide thin films were deposited by reactive DC magnetron sputtering in a coating system based on a Balzers UTT 400 unit. The substrates were unheated during the entire deposition process. The substrates were glass plates with transparent and electrically conducting layers of In_2O_3 (ITO) having a sheet resistance of $60\ \Omega$. Samples were also deposited onto carbon substrates for composition determination by Rutherford Backscattering Spectrometry (RBS). The target was a 5-cm-diameter plate of metallic nickel (99.995%). Prior to deposition, the chamber was evacuated to $\sim 10^{-7}$ Torr. Pre-sputtering took place in argon–oxygen atmosphere for five minutes before sample fabrication. The sputtering power was kept at 200 W and the pressure in the chamber was maintained at ~ 30 mTorr during the whole process. Ni oxide thin films with different oxygen content were obtained by adjusting the oxygen/argon ratio from 2 to 10%.

Film structures were determined by x-ray diffraction using a Siemens D5000 diffractometer operating with CuK_α radiation at a wavelength 0.154 nm and elemental compositions were determined by RBS; data are given in our earlier paper.^[15] Film thicknesses were measured to be 280–300 nm by use of a DektakXT instrument. Surface morphologies were recorded by scanning electron microscopy using a LEO 1550 FED Gemini instrument with an acceleration voltage of 10–15 kV.

Cyclic voltammetry (CV) was performed in a three-electrode electrochemical cell by use of a computer-controlled ECO Chemie Autolab/GPES Interface. The Ni oxide film served as

working electrode and was electrochemically cycled in 1M LiClO₄ in propylene carbonate. Li foils were used as counter and reference electrodes. All electrochemical studies were performed in an argon-filled glove box with water content below ~0.5 ppm. The electrolyte was prepared by dissolving LiClO₄ in propylene carbonate inside the glove box. Both chemicals were fresh and moisture free. Extended CV cycling was carried out at a scan rate of 50 mV s⁻¹. Charge density C_e (in units of mC cm⁻²) was determined from cyclic voltammetry data by $C_e = \int j dV/s$, where j is current density (in mA cm⁻²), s is scan rate (in V s⁻¹), and V is voltage (in V).

Optical transmittance was recorded *in situ* during electrochemical cycling in the 380–800 nm wavelength range by using a fiber-optical instrument from Ocean Optics. The electrochemical cell was placed between a tungsten halogen lamp and the detector, and the 100%-level was taken as the transmittance recorded before putting the sample in the electrolyte.

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Table 1. Parameters used to fit the expressions for a power law (Eq. 1) and a stretched exponential (Eq. 2) to experimental data on the decay of charge density for coloration upon voltammetric cycling. The value A is the same for both equations, and is governed by the first cycle.

	Potential range (V)	A	Power law (Eq. 1)			Stretched exponential (Eq. 2)		
			B_1	x_{01}	p_1	B_2	x_{02}	p_2
NiO _{1.16}	2.0–3.7	0.914	0.60252	23.59	0.8004	0.61656	20.18	0.5984
	2.0–4.1	2.113	1.74399	93.85	0.5126	1.80341	52.17	0.4385
	2.0–4.4	2.460	1.66543	17.42	0.5778	1.75814	10.40	0.4344
	2.0–4.7	3.768	2.60798	5.99	0.5702	2.43311	3.48	0.4146
NiO _{1.25}	2.0–3.7	1.073	0.69039	61.27	0.6515	0.73054	42.09	0.4928
	2.0–4.1	2.603	1.54124	42.26	0.6362	1.64031	29.06	0.4665
	2.0–4.4	3.960	2.34575	15.24	0.4959	2.56147	7.75	0.3800
	2.0–4.7	5.495	2.46905	14.19	0.3628	2.95546	5.96	0.2999
NiO _{1.32}	2.0–3.7	2.175	0.90302	61.96	0.5443	1.05992	35.69	0.4187
	2.0–4.1	3.787	1.74508	103.37	0.6060	2.02161	63.42	0.4827
	2.0–4.4	5.551	2.63233	24.80	0.5803	3.0382	15.75	0.4766
	2.0–4.7	5.264	3.14196	9.91	0.5069	3.43684	5.92	0.4121

Figure 1. Spectral transmittance of a ~290-nm-thick $\text{NiO}_{1.16}$ film in as-deposited state and after bleaching and coloring at the shown potentials vs. Li/Li^+ . Data correspond to the second CV cycle at a scan rate of 50 mV s^{-1} . Bleached films display overlapping spectra.

Figure 2. (a)–(c) Cyclic voltammograms and (a')–(c') corresponding optical transmittance spectra for ~290-nm-thick Ni oxide films with the stated compositions. Data were taken for 2.0–4.1 V vs. Li/Li⁺ at 50 mV s^{−1}, and spectra correspond to endpoints of the voltammetric cycles for films in as-deposited state and after the indicated numbers of cycles. The scan started at ~3.25 V vs. Li/Li⁺.

Figure 3. Cyclic voltammograms for ~290-nm-thick Ni oxide films of the shown compositions in 1M LiClO₄-PC, recorded for the potential ranges 2.0–4.4 (panels a–c) and 2.0–4.7 V vs. Li/Li⁺ (panels a'–c') at 50 mV cm⁻¹. The scan started at ~3.25 V vs. Li/Li⁺.

Figure 4. Charge density for coloration upon voltammetric cycling of ~290-nm-thick Ni oxide films with the stated compositions pertaining to the columns of panels, shown with logarithmic scales on both axes. The various rows of panels refer to the indicated potential ranges vs. Li/Li^+ . Symbols denote experimental data and curves were drawn as fits to models representing a power law (Eq. 1) and a stretched exponential (Eq. 2) using parameters reported in Table I and partly given also in Figure 7. The fitted data overlap.

Figure 5. Charge density for coloration upon voltammetric cycling of ~290-nm-thick Ni oxide films with the stated compositions pertaining to the columns of panels, shown with linear scales on both axes. The various rows of panels refer to the indicated potential ranges vs. Li/Li⁺. Symbols denote experimental data for coloration and bleaching.

Figure 6. Difference in charge density δQ between coloration and bleaching upon voltammetric cycling of ~ 290 -nm-thick Ni oxide films with the stated compositions for the indicated potential ranges vs. Li/Li^+ . Symbols denote experimental data, which were connected by straight lines for clarity.

Figure 7. Exponents p_1 and p_2 from fitting the *power-law* and *stretched-exponential* degradation models in Equations (1) and (2), respectively, to experimental data on charge density decay upon extensive electrochemical cycling, using a lower potential limit of 2.0 V vs. Li/Li⁺, for Ni oxide films with the shown compositions.

Figure 8. Charge density decline during extended electrochemical cycling of ~290-nm-thick NiO_{1.32} films, recorded for the potential ranges (a) 2.0–4.4 and (b) 2.0–4.7 V vs. Li/Li⁺. Vertical lines separate different stages of decay, as discussed in the main text. Scanning electron micrographs are shown for (c) an as-deposited film, (d) after 2000 cycles at 2.0–4.4 V vs. Li/Li⁺, and after (e) 800, (f) 1300, and (g) 2000 cycles at 2.0–4.7 V vs. Li/Li⁺. The latter image shows nothing but ITO. The scale bar is 200 nm.

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Degradation kinetics: a rapid drop of charge density during the first hundreds of cycles and a subsequent slower decline. The decay is independent of film composition and applied potential range as long as the upper limit of the potential is ≤ 4.4 V vs. Li/Li⁺. The degradation kinetics can be modeled by a *power law* or, alternatively, a *stretched exponential*.