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Degradation Dynamics for Electrochromic WO₃ Films under Extended Charge Insertion/Extraction: Unveiling Physicochemical Mechanisms

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ABSTRACT

Degradation of electrochromic thin films under extended charge insertion/extraction is a technically important phenomenon for which no in-depth understanding is currently at hand. Here we report on an explorative study of sputter-deposited WO₃ films in a Li-ion-conducting electrolyte by use of cyclic voltammetry, *in situ* optical transmittance, and impedance spectroscopy. A cycling-dependent decrease of the charge capacity could be accurately modeled by a power-law function, and impedance spectroscopy gave evidence for anomalous diffusion as well a higher charge transfer resistance during deintercalation than during intercalation. Thus a consistent conceptual picture emerged for the degradation dynamics; it includes the growth of an interfacial barrier layer and also embraces anomalous diffusion coupled with dispersive power-law chemical kinetics.

Keywords: WO₃, thin films, electrochromism, de-trapping, physicochemical mechanisms

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1. INTRODUCTION

Devices relying on reversible ion intercalation are used in sustainable energy technology, for example in rechargeable electrical batteries^{1, 2} and electrochromic (EC) glazings for energy-efficient buildings with good indoor comfort.^{3, 4} This paper deals with EC devices, whose optical properties can be changed between transparent and absorbing states by the application of a voltage of the order of a few volts. Specifically, we discuss amorphous WO_3 , which is the most widely studied EC material ever since the discovery of electrochromism more than 40 years ago;⁵ thin films of WO_3 also constitute the main optically functional part in today's commercial EC "smart windows".⁶

WO_3 -based EC devices suffer from diminished optical modulation upon long-term electrochemical cycling, which is connected with the difficulty to extract all of the inserted ions. This phenomenon leads to ion accumulation in the host structure and thereby to a loss of device efficiency.⁷⁻¹⁰ However, we recently discovered that WO_3 films that had been degraded in a Li-ion-conducting electrolyte were able to regain their initial performance through galvanostatically^{7, 8, 10} or potentiostatically^{10, 11} induced processes involving ion traps. Similar device rejuvenation is possible for TiO_2 -based¹¹ and MoO_3 -based¹² EC films.

In crystalline WO_3 , the inserted Li ions are located at well-defined vacant positions between WO_6 octahedra and bond to adjacent oxygen atom(s). Amorphous WO_3 , on the other hand, exhibits structural disorder implying broken bonds and varying bond lengths, bond angles and coordinations.¹³ Inserted Li ions can then bond more or less strongly to one or more oxygens in distorted WO_z polyhedra and give rise to a wide distribution of binding energies. Hence site-dependent activation energies have to be overcome if the ions are to be released, which curtails the reversibility of this process. During each ion intercalation/deintercalation half-cycle, a small amount of the ions may bond at sites with a

high binding energy and become trapped there—*i.e.*, inaccessible for extraction in the subsequent half-cycle—so that reversibility is lost and charge capacity, and hence optical modulation, are reduced. Accumulation of trapped ions may also result in structural modification and compositional changes upon cycling.

Ion trapping in oxides is an interesting and poorly understood phenomenon with obvious bearing on the service lifetime of EC devices, and the purpose of our present study is to unveil some underlying physicochemical mechanisms for Li ion trapping in WO₃ films by combining data from optical transmittance recordings, cyclic voltammetry, and impedance spectroscopy. In addition, we show that degradation dynamics can be accurately characterized by a power law.

2. EXPERIMENTAL SECTION

WO₃ films were prepared as in earlier studies of ours.⁷⁻¹⁰ Depositions were carried out by reactive DC magnetron sputtering. Glass plates, pre-coated with In₂O₃:Sn (ITO, 60 Ω /square), were used as substrates. The sputter target was a 5-cm-diameter plate of metallic tungsten (99.95%). The sputtering chamber was first evacuated to $\sim 6 \times 10^{-5}$ Pa and pre-sputtering took place in argon (99.998%) and oxygen (99.998%) for a few minutes. The substrate was unheated, and film uniformity was ensured by substrate rotation. The oxygen/argon gas-flow ratio and sputtering power were maintained at 13 to 16% and 200 to 230 W, respectively. The pressure in the sputter plasma was set to values in the 20–40 mTorr interval in order to obtain films with different nanostructures and porosities. Film densities were in the range of 5.0 to 6.0 g cm⁻².^{9, 14} Film thicknesses were determined by surface profilometry, using a DektakXT instrument. The WO₃ films were amorphous as inferred from x-ray diffractograms which showed nothing but features from the underlying ITO coatings.

Electrochemical measurements were performed with an ECO Chemie Autolab/GPES Interface. Cyclic voltammetry (CV) data were recorded at voltage scan rates of 20 or 50 mV s⁻¹ in an argon-filled glove box, whose water content was below ~0.5 ppm, using a three-electrode electrochemical cell. The working electrode was the WO₃ film, which was electrochemically cycled in an electrolyte of 1M LiClO₄ dissolved in propylene carbonate (PC). The counter and reference electrodes consisted of Li foil. Charge capacity Q was obtained from CV data by $Q = \int (J dV)/s$, where the integration was performed over a voltammetric half-cycle corresponding to either charge insertion or charge extraction; J is current density, V is voltage, and s is voltage scan rate.

In situ optical transmittance was measured concurrently with the CV recordings in the 400–800 nm wavelength range, corresponding to visible light, by use of an Ocean Optics fiber-optical instrument. 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.

Impedance spectroscopy was performed in the frequency range from 100 kHz to 0.01 Hz by use of a Solartron 1260 Frequency Response Analyzer together with a Solartron 1286 Electrochemical Interface and using the same experimental arrangements as for the CV recordings.¹⁴ Measurements were performed with a DC bias potential and a superimposed AC voltage of 10 mV. The samples were kept at each potential for 15 minutes, in order to ensure stable conditions, before acquiring an impedance spectrum. The duration of the spectrum measurement was 20–30 minutes at each potential.

3. RESULTS AND DISCUSSION

Figure 1A reports cyclic voltammetry data for a ~300 nm-thick WO_3 film immersed in the $\text{LiClO}_4\text{-PC}$ electrolyte and demonstrates that the area enclosed by the curves shrinks continuously during cycling, implying decreased ion intercalation capacity of the films as cycling proceeds. The overall CV curves are also significantly shifted towards lower voltages upon increasing cycle number x , indicating that intercalation is increasingly impeded at higher cycle numbers.

Figure 1. Electrochemical and electrochromic performance in $\text{LiClO}_4\text{-PC}$ of a ~300-nm-thick WO_3 film, deposited at a pressure of 30 mTorr and an O_2/Ar gas-flow ratio of 0.13. (A) Cyclic voltammograms recorded at a voltage scan rate of 20 mV s^{-1} after the indicated numbers of cycles; long arrows indicate voltage sweep direction. (B) Charge capacity degradation upon electrochemical cycling to insert or extract charge according to (A); symbols denote experimental results on inserted and extracted charge, and the curve was obtained from Equation 1 with parameters given in Table 1 (row 1). (C) Evolution of optical transmittance modulation recorded at a wavelength of 550 nm; data up to ~300 h mirror the charge capacities in (B), and subsequent optical data illustrate the effect of

galvanostatic rejuvenation followed by another round of electrochemical cycling; selected time-resolved optical transmittance data are shown in the inset of **(B)**. **(D)** Open-circuit potential (OCP) *vs.* cycle number, showing experimental results and a curve computed from Equation 2 using parameters reported in the main text; selected OCP data are indicated by short vertical arrows in **(A)**.

Data such as those in **Figure 1A** were integrated in order to obtain inserted/extracted charge during each CV cycle, as reported in **Figure 1B**. Clearly the charge capacity decreases monotonically from 27.5 to 7.5 mC cm⁻² as x goes from 1 to 5500, and a decline is still apparent at the largest cycle number. Data for inserted and extracted charge during a CV cycle are indistinguishable except for a minuscule difference for the first cycle. **Figure 1C** illustrates the corresponding evolution of the optical transmittance modulation at a mid-visible wavelength of 550 nm, and the inset in **Figure 1B** gives snapshots of the modulation for the first and 5500th CV cycle (recorded after ~300 h). The dark-state transmittance increases from ~15 to ~60% concurrently with the drop of the charge capacity while the bleached-state transmittance remains at ~90%, which is in accordance with earlier results.^{7, 8, 10}

After 5500 CV cycles, the WO₃ sample was subjected to galvanostatic rejuvenation as previously described by us.^{7, 8} This was accomplished by running a constant current of $\sim 3 \times 10^{-6}$ A cm⁻² through the sample for 7 h in the “bleaching direction”, which made the voltage on the sample increase to ~5.5 V *vs.* Li/Li⁺. **Figure 1C** indicates that this procedure brought back the initial optical properties of the WO₃ film and that subsequent CV cycling led to a loss of optical modulation that is similar—albeit somewhat faster—than that of the first round of CV cycling. The outcome of this rejuvenation procedure is consistent with recent observations.⁸

In order to describe and understand the decay of the electrochromism, it is necessary to fit the CV-cycle-dependent decrease of the charge capacity to a physically-motivated model.

Following earlier work on EC Ni oxide films,¹⁵⁻¹⁷ we adopt a power-law model which can be fitted to the data in **Figure 1B** by using an asymptotic value of Q not significantly different from zero. A stretched-exponential model might also be used,^{16, 17} but this representation requires non-zero asymptotic charge capacity in the case of our films, which we consider to be unlikely since no physicochemical mechanism prevents the film from eventually losing all of its charge capacity and become electrochemically inactive. Hence the stretched-exponential representation would necessitate one more parameter than the power-law model and is undesirable also for this reason. Both the power-law and stretched-exponential model can be justified in terms of first- and second-order chemical reactions.^{16, 18}

Based on the arguments above, the data on charge capacity in **Figure 1B** were fitted to the equation

$$Q(x) = \frac{A_Q}{1 + \left(\frac{x-1}{x_{0Q}}\right)^{p_Q}} \quad , \quad (1)$$

where A_Q is the initial charge capacity, x_{0Q} is the cycle number at which the charge density has declined to half of its final value, and p_Q is a kinetic exponent. We used parameters in **Table 1** (row 1) and found that the model represented the measured results very accurately. Charge capacity evolution was studied also for four more WO_3 samples, reported on in **Figure 2** and **Table 1** (rows 2–5), prepared by deposition at the shown pressures in the sputter plasma and subjected to the indicated numbers of CV cycles at the shown voltage scan rates. Corresponding experimental and fitted data are reported in **Figure 2** and verify that the power-law model works well. The initial charge capacity displayed a clear dependence on the pressure during sputtering, which is apparent from the data in **Table 1** (rows 2–4). The value of A_Q rises in proportion with the pressure in the sputter plasma, which is as expected and consistent with higher deposition pressures giving increasingly porous WO_3 films^{19, 20} thus enabling more ion intercalation/deintercalation. In addition the value of x_{0Q} decreases with

increasing deposition pressure, as seen in Table 1 (rows 2-4). This implies that the more porous films deposited at high pressure during sputtering exhibit a significantly faster degradation. The kinetic exponent is considerably larger than the semi-infinite diffusion value of 0.5, and p_Q lay in the range of 0.73–0.94 with no clear dependence on deposition pressure.

Table 1. Data for ~300-nm-thick WO_3 films in $\text{LiClO}_4\text{-PC}$, subjected to cyclic voltammetry for the indicated number of cycles at the shown voltage scan rates. Thin-film depositions were performed at the stated pressures in the sputter plasma. Parameters A_Q , x_{0Q} , and p_Q were used to fit experimental data to the power-law model encapsulated in Equation 1.

Number of cycles	Scan rate (mV s^{-1})	Pressure (mTorr)	A_Q (mC cm^{-2})	x_{0Q}	p_Q
5500	20	30	26.65	1341	0.73
500	20	40	39.75	500	0.94
500	20	30	29.94	739	0.83
500	20	20	22.09	1647	0.86
1000	50	30	15.64	3100	0.73

Figure 2. Charge capacity evolution of ~300-nm-thick WO_3 films in $\text{LiClO}_4\text{-PC}$. The films were deposited at the shown pressures in the sputter plasma and were subjected to cyclic voltammetry at 2.0–4.0 V *vs.* Li/Li^+ for the indicated voltage scan rates. A smaller number of CV cycles was used for the lower rate in order to avoid excessive time for the experiment. Experimental data were fitted to the power-law model represented by Equation 1 by use of the parameters listed in Table 1 (rows 2–5).

The CV data in **Figure 1A** indicate a monotonic overall shift towards lower voltages. This feature was quantified in terms of open-circuit voltages (OCPs), *i.e.*, potentials at which the current density began to depart from zero in the negative scan direction. OCPs are usually defined as electrode potentials under open-circuit conditions; here this concept is generalized and applies to the individual voltammograms. **Figure 1D** shows that the OCP shifts monotonically from ~3.5 to ~2.8 V *vs.* Li/Li^+ as the number of CV cycles is increased to 5500.

The variation of the OPV could be modeled by a power law, specifically by the expression

$$V_{\text{OPV}}(x) = B_{\text{OPV}} + \frac{A_{\text{OPV}} - B_{\text{OPV}}}{1 + \left(\frac{x-1}{x_{0\text{OPV}}}\right)^{p_{\text{OPV}}}}, \quad (2)$$

which makes the functional dependence analogous to that of the decrease in the charge capacity. Here A_{OPV} is the initial value of the OCP, and B_{OPV} is the residual OCP after long-term CV cycling (which obviously must lie within the potential limits in the experiment and hence be non-zero); furthermore $x_{0\text{OPV}}$ is the cycle number at which the decline in OCP has reached half of its final value, and p_{OPV} is an exponent. **Figure 1D** shows data obtained from **Equation 2** and demonstrates that the power law is in excellent accord with the experimental results; specifically, the fitting used $A_{\text{OPV}} = 3.483 \text{ V}$, $B_{\text{OPV}} = 2.451 \text{ V}$, $x_0 = 2711$, and $p_{\text{OPV}} = 0.52$. We note, in passing, that the power-law representation is not unique, and a stretched-exponential model is able to produce an indistinguishable fit.

We now turn to impedance spectroscopy in order to elucidate the physical mechanisms that may be responsible for the decline of charge capacity and the shift of OCP during extended CV cycling. Data were collected during a single CV cycle. Measurements started at 3.3 V *vs.* Li/Li⁺ and ion intercalation was studied at a number of successively lower potentials down to 1.0 V *vs.* Li/Li⁺; subsequently ion deintercalation was probed analogously as the potential was increased to 3.0 V *vs.* Li/Li⁺. Recordings lasted for almost an hour at each potential and therefore led to more severe ageing than during one rapid CV cycle. Indeed, impedance spectroscopy demonstrated that the charge capacity during ion deintercalation was much smaller than during intercalation, which indicates that differences between impedance spectra taken during intercalation and deintercalation can give information on degradation mechanisms. **Figure 3A** reports imaginary *vs.* real impedance for a WO₃ film subjected to ion intercalation/deintercalation at a potential of 2.0 V *vs.* Li/Li⁺. Both sets of data show that the real and imaginary parts of the impedance increase monotonically as the frequency is lowered, in the range below 100 kHz for ion intercalation and below ~500 Hz for ion deintercalation. During ion deintercalation the real part of the impedance shifted towards larger values, which signals an increase of the sample resistance. Furthermore, the low-frequency (< 1 Hz)

impedance recorded during deintercalation (not shown) was much higher than during intercalation and was dominated by a resistive behavior.

Figure 3. Impedance spectroscopy data recorded in $\text{LiClO}_4\text{-PC}$ for a $\sim 100\text{-nm}$ -thick WO_3 film deposited at a pressure of 20 mTorr and an O_2/Ar gas-flow ratio of 0.16. **(A)** Imaginary vs. real parts of the impedance measured at the shown potential during ion intercalation/deintercalation (selected frequencies are indicated); data points denote measured results and solid curves are fits to an extended Randles circuit. **(B)** Randles-type circuit wherein R_{ohm} is electrolyte resistance, R_{ct} is charge transfer resistance, CPE_{dl} is double-layer constant phase element, Z_{AD} denotes impedance of an anomalous diffusion element, and R_{sr} is a parasitic resistance. **(C)** Charge transfer resistance and **(D)** anomalous diffusion exponent vs. potential derived from impedance spectroscopy data analogous to those in **(A)**; data points are joined by straight lines for convenience.

The spectra in **Figure 3A** were fitted to a Randles circuit²¹ extended to include anomalous diffusion kinetics,^{22, 23} as illustrated in **Figure 3B**. Here R_{ohm} is the resistance of

the electrolyte, and the properties of the film–electrolyte interface are represented by a charge transfer resistance R_{ct} and a double-layer constant phase element denoted CPE_{dl} . Z_{AD} refers to an anomalous diffusion element, specifically Bisquert and Compte’s circuit element type ADIb with reflecting interface, whose characteristics were derived from equations describing fractional diffusion.²² The pertinent frequency-dependent impedance is

$$Z_{AD}(j\omega) = \Phi(\omega_d/j\omega)^{1-\gamma/2} \coth[(j\omega/\omega_d)^{\gamma/2}], \quad (3)$$

where Φ is a pre-factor,²² γ is an anomalous-diffusion exponent, and $\omega_d = (D/L^2)^{1/\gamma}$ with D being the Fickian diffusion coefficient and L the film thickness. Finally, R_{sr} is a series resistance due to possible side reactions; it had finite values at all potentials during ion deintercalation but only at potentials below 2.0 V vs. Li/Li⁺ during intercalation. **Figure 3A** demonstrates excellent agreement between experimental data and calculations based on the extended Randles circuit.

Fittings of impedance spectra yielded voltage-dependent values of R_{ct} and γ as reported in **Figures 3C** and **3D**, respectively. Data were obtained also for the other circuit elements, but they are of less interest here. Two features stand out from the analysis: the charge transfer resistance is significantly higher at all potentials during ion deintercalation than during the preceding intercalation, and the anomalous diffusion coefficient has only a modest dependence on potential during intercalation and lies consistently in the 0.58–0.80 interval. The value of γ is uncertain during ion deintercalation and is strongly influenced by the magnitude of R_{sr} . **Figure S1** shows impedance spectroscopy data for a WO₃ film prepared under different conditions and studied in the narrower potential range of 2.0–3.3 V vs. Li/Li⁺. This latter film did not exhibit any significant decrease of charge capacity during impedance measurements, and the anomalous diffusion behavior was closely similar during ion intercalation and deintercalation (**Figure S2**). However, the charge transfer resistance was

clearly increased during ion deintercalation (**Figure S3**), which is interpreted as a sign of incipient degradation.

We are now in a position to discuss degradation mechanisms during electrochemical cycling of WO_3 films and first consider the shift of the OCP towards lower values (**Figure 1D**). This effect can ensue from two mechanisms and be associated with (i) the increased charge transfer resistance, and (ii) the fact that the OCP is sensitive to the surface state of the film as shown recently for $\text{SnO}_2\text{:Sb}$.²⁴ Irrespective of mechanism, we hypothesize that the underlying cause of the altered OCP is the growth of an *interfacial barrier layer* that impedes ion transport (possibly akin to a cathode/electrolyte interphase,²⁵ which is a phenomenon that has been studied in battery technology).

We also believe that the power-law kinetics inherent in **Equations 1** and **2** may be due to *diffusion-limited chemical reactions*. The reasons for this belief are based on the fact that the kinetic exponents p_Q are similar to the anomalous diffusion coefficients in **Figure 3D**, in particular if one considers only the most accurate data obtained by fitting to 5500 CV cycles. Our arguments are founded on analyses of dispersive chemical kinetics by Plonka^{18, 25} who showed that **Equation 1** follows from a second-order rate equation using a time-dependent rate constant¹⁸

$$k(t) \sim t^{p_Q-1} . \quad (4)$$

For a diffusion controlled reaction, the exponent of the rate constant can be interpreted as a diffusion exponent within the so called Continuous-Time Random-Walk (CTRW) model.²⁶ Specifically, the rate constant can be obtained from^{25,27}

$$k(t) \sim \frac{ds(t)}{dt} \sim \frac{dt^\gamma}{dt} \sim t^{\gamma-1} , \quad (5)$$

for a CTRW with the well-established waiting-time distribution^{26,27} $\sim t^{-\gamma-1}$. In eq. (5), $S(t)$ is the mean number of distinct sites visited by a diffusing particle at time t . It has been shown²³ that a CTRW model with such a power-law distribution of waiting times obeys the same fractional-diffusion equation^{22,23} as the model for anomalous diffusion in eq. (3), that was used for the fits leading to **Figures 3D** and **S2**. These arguments hence imply that $p_Q = \gamma$, and clearly support our surmise that diffusion-limited reactions govern the degradation kinetics of the EC properties, but we admit that our chain of arguments is rather tenuous.

4. CONCLUSIONS

We reported data from an explorative study on the long-term evolution of the electrochromic properties of tungsten oxide films undergoing repeated charge insertion/extraction. The decline of the charge capacity with increasing cycle number was fitted to a power-law model. The key result is the emergence of a consistent conceptual framework for explaining the degradation dynamics, including the growth of an interfacial barrier layer and with notions based on anomalous diffusion coupled with dispersive chemical kinetics. These insights can constitute a starting point for more detailed experimental and theoretical investigations.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Impedance spectroscopy, anomalous diffusion and charge transfer resistance data.

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Table of Contents (TOC) graphic