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ANOMALOUS DIFFUSION OF IONS IN ELECTROCHROMIC TUNGSTEN OXIDE FILMS

Sara Malmgren¹, Sara V. Green² and Gunnar A. Niklasson*

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

¹Present address: Swedish Energy Agency, P.O. Box 310, SE-63104 Eskilstuna, Sweden

²Present address: Exeger Sweden AB, P.O. Box 55597, SE-10204 Stockholm, Sweden

Abstract

Amorphous tungsten oxide thin films were deposited by sputtering at different O₂/Ar ratios onto conducting substrates. Ion intercalation and diffusion in the films was studied by electrochemical impedance spectroscopy measurements in the frequency range 10 mHz-100 kHz and for potentials between 1.0 and 3.2 V vs. Li/Li⁺, using the film as working electrode in a Li⁺ containing electrolyte. The impedance data were in very good agreement with anomalous diffusion models. Different models were found to be applicable at potentials >1.8 V and <1.8 V. At high potentials ion intercalation was found to be reversible and an anomalous diffusion model describing ion hopping was favored. At low potentials ion intercalation was found to be irreversible and ion trapping takes place. In this latter range an anomalous diffusion model for the case of non-conserved number of charge carriers gave the best fit to experimental data. We obtained potential dependent diffusion coefficients in the range from 10⁻⁹ to 10⁻¹¹ cm²/s, and anomalous diffusion exponents in the range 0.1 to 0.4, with the films deposited at lower O₂/Ar ratios exhibiting the higher values.

Keywords: Electrochromism, impedance spectroscopy, anomalous diffusion, tungsten oxide

*Corresponding author

1. Introduction

The optical properties of electrochromic materials can be reversibly changed by the application of an electrical signal [1-3]. This makes it possible to vary the transmittance of solar radiation which constitutes the basic principle for energy-efficient “smart window” technology [4,5]. An electrochromic device consists of a cathodic and an anodic electrochromic coating separated by a solid electrolyte and sandwiched between transparent electrical contact layers. The most used cathodic electrochromic material is tungsten oxide (WO_3), which exhibits an intervalence charge transfer absorption [6] in the visible and near-infrared regions, upon intercalation by protons or Li^+ ions from the electrolyte [7,8]. Hence the optical switching is intimately related to the kinetics of ion insertion and ion diffusion in the coating. Impedance spectroscopy is a convenient method for studying ion diffusion mechanisms in electrochromic materials [9,10] and it may also be used as a non-destructive method to detect ageing during electrochemical cycling between transparent and colored states [11].

Diffusion of ions from an electrolyte into a solid material is also of importance for a number of other technological applications, for example Li^+ ion batteries [12]. The dynamics of the process is however complicated and depends on the nanostructure of the solid as well as on the properties of the electrolyte-electrode interface and – in the case of a thin film electrode – the back contact to the film. The dynamics can, to a fair approximation, be described by a so called Randles circuit [13], where the ordinary ion diffusion gives rise to a characteristic frequency dependence of the impedance spectrum. However, the Randles model is often too simple and needs to be extended to accurately describe experimental data. In particular, the physics of so called anomalous diffusion [14,15] has attracted a large interest. Bisquert and Compte [16] explored the consequences of anomalous diffusion in electrochemical systems and derived analytical results and equivalent circuits, where the diffusion impedance was represented by transmission line circuits. Different

types of anomalous diffusion were found [16], which can be derived from different fractional diffusion equations [17], describing the fractal dynamics of ion transport. Depending on whether the number of charge carriers is taken to be conserved or not, the anomalous diffusion models have a strong connection to hopping and trapping models describing charge transport in disordered materials [17]. Fractional equations of motion are also of fundamental interest, since they represent a consistent way to describe irreversible phenomena, where the “arrow of time” appears in a natural way [18].

In this paper, we present an experimental verification of the fractional diffusion models. We report impedance spectroscopy measurements on amorphous tungsten oxide films under conditions of ion intercalation from an electrolyte containing Li^+ ions. An original feature of our work is that we consider the rarely studied potential range of irreversible ion intercalation as well as the range of reversible ion intercalation. We find that different anomalous diffusion models are applicable for the cases of reversible and irreversible ion intercalation. These models are corresponding to ion hopping and ion trapping processes, respectively.

2. Experimental

Thin films of tungsten oxide (WO_3), were prepared using reactive DC magnetron sputtering onto unheated substrates. Glass substrates coated with conducting $\text{In}_2\text{O}_3:\text{Sn}$ (ITO; $10\ \Omega/\text{square}$) were used for impedance spectroscopy and glassy carbon substrates for compositional characterization. A multi target sputter system, based on a Balzers UTT 400 unit, was used with 99.95% pure metallic 5 cm diameter W targets positioned 13 cm from the substrates. The deposition took place in a 99.995% pure argon–oxygen atmosphere at a pressure of 20 mTorr and without substrate heating. The O_2/Ar flow ratios used were between 0.16 and 0.70 and the sputtering power was 200 W during deposition of WO_3 . Film thicknesses were determined to be in the range 90–110 nm, using an Alpha

Step profilometer. The films were found to be X-ray amorphous, in agreement with our earlier findings that a substrate temperature in excess of 250°C is needed to induce crystallinity [19]. Analysis by Rutherford Backscattering Spectrometry (RBS) gave densities in the range of 5.0 to 5.7 g/cm². The RBS compositional analysis did not show significant departures from the stoichiometric WO₃ composition, but previous measurements with Elastic Recoil Detection Analysis [19] gave evidence for a slightly substoichiometric composition of films produced at the lowest O₂/Ar ratios.

Electrochemical measurements were performed using a standard three-electrode setup with the film under study as working electrode, and lithium foils as counter and reference electrodes, all submerged in an electrolyte consisting of 1 M LiClO₄ in propylene carbonate. Impedance spectroscopy was performed using a Solartron 1260 frequency response analyzer together with a Solartron 1286 electrochemical interface. Complex impedance spectra were recorded using a 10 mV amplitude ac potential between 10 mHz and 100 kHz with 10 points per decade and at various applied dc potentials. The first impedance spectrum was taken at 3.2 V and thereafter the potential was gradually decreased in steps with the final spectrum taken at 1.0 V vs. Li/Li⁺. Subsequently further measurements were taken at increasing potentials up to 3.2 V vs. Li/Li⁺. Random errors were minimized by integration over three cycles at each frequency. Spectra at different potentials were recorded after applying each potential for 900 s, allowing the Li content in the films to approach a steady state. At the end of the pretreatment, the current change per minute was lower than 0.1 μA/cm². To study special phenomena, supplementary measurements were taken on some samples in a narrower potential range than the one given above.

It should be mentioned that basic electrochemical and optical characterization of thin films sputtered at the same and similar conditions as those in the present paper has been previously reported by our group. Specifically, optical absorption, cyclic voltammetry and electrochromism has been studied in detail as a function of deposition conditions [20] and it was found that

electrochemical and optical properties were qualitatively similar in a wide window of sputtering conditions. In addition, the optical absorption has been thoroughly characterized in both regimes of reversible and irreversible ion intercalation [21]. Our recent studies by Elastic Recoil Detection Analysis (ERDA) [22] and Secondary Ion Mass Spectroscopy (SIMS) [23] have conclusively shown that Li ions are intercalated electrochemically into WO₃ films and that a significant amount of Li ions are irreversibly trapped in the films at low potentials around 1.5 V.

3. Theory

The impedance response due to ion transport in electrochromic tungsten oxide was first analyzed by Ho et al. [9], who solved the diffusion equation for a thin film in contact with an electrolyte. The impedance was shown to be due to interfacial charge transfer and ion diffusion processes, and could be represented by a Randles equivalent circuit [9,13]. More recently extensions of this theory have been proposed to take into account a possible fractal dynamics of the ion transport. To this end fractional diffusion equations were obtained by generalizing either Fick's law or the continuity equation [16] and the solution of these equations lead to different anomalous diffusion theories [16,17]. Fig. 1a shows a generalized Randles circuit where the ordinary diffusion element has been replaced by an anomalous diffusion (Z_{AD}) element. The circuit contains an electrolyte resistance, R_{ohm} , an interfacial charge transfer resistance, R_{ct} , a double layer constant phase element, CPE_{dl} , and the distributed anomalous diffusion element. The Z_{AD} element in the circuit can be visualized by a transmission line, as illustrated in Fig. 1b; its impedance is equal to [16]

$$Z_{AD}(j\omega) = (\zeta_m \chi_m)^{1/2} \coth \left[L \left(\frac{\chi_m}{\zeta_m} \right)^{1/2} \right], \quad (1)$$

where L is the film thickness, χ_m is an impedance per unit length (Ωm^{-1}) and ζ_m is an impedance-

length (Ωm).

Two anomalous diffusion models denoted AD1a and AD1b are of interest for the present study. The AD1a model involves a fractional generalization of the continuity equation, and hence the number of diffusing ions is not conserved [16]. Furthermore, the model can be derived from multiple trapping in an exponential density of states [17]. On the other hand, in the AD1b model the number of diffusing ions is conserved and instead the constitutive diffusion equation is generalized [16]. The AD1b result can also be obtained from a Continuous Time Random Walk model [17], commonly used to describe transport in disordered materials. As illustrated in Fig. 1c, in the case of AD1a, χ_m is a resistance/length and ζ_m is a CPE-length, while in AD1b χ_m is a CPE/length and ζ_m denotes the impedance-length of a capacitor [16], $1/j\omega\epsilon_m$. For ordinary diffusion χ_m is a resistance/length and ζ_m the impedance-length of a capacitor.

The impedance of a CPE can be written as

$$Z_{CPE}(j\omega) = q_m (j\omega)^{-n}, \quad (2)$$

where n is the CPE exponent and q_m the distributed CPE prefactor. The exponent $n=0$ corresponds to a resistance and $n=1$ to a capacitive behaviour. The CPE's are denoted by their prefactors in Fig. 1c.

In order to study the physics of ion transport in tungsten oxide, it is of prime importance to analyze the Z_{AD} element. It has three fitting parameters but two of them can be combined to obtain the diffusion coefficient of the ions. The third fitting parameter is the AD exponent, n . As discussed before [22], the diffusion coefficient (in units of m^2/s^{1-n}) in the fractional diffusion equations of

Bisquert and Compte [16] must be modified in order to be presented in the correct units, i.e. in m^2/s .

We can obtain an effective ion diffusion coefficient in the film by using the basic relation,

$$D_{eff} = L^2 \omega_d , \quad (3)$$

where ω_d is the characteristic frequency of diffusion. We then combine eq. (3) with the AD relations for ω_d obtained previously [16]. Within the AD1b model we find [24]

$$\omega_d = (c_m q_m L^2)^{-1/(1-n)} , \quad (4)$$

where c_m is the capacitance per unit length of the ζ_m element and the parameters q_m and n pertain to the χ_m element. The effective diffusion coefficient within the AD1a model can be obtained in analogy with eq. (4) from [16]

$$\omega_d = (q_m / r_m L^2)^{1/(1-n)} , \quad (5)$$

where r_m is the diffusion resistance per unit length and the parameters q_m and n now pertain to the ζ_m element.

4. Results and discussion

Figure 2 shows experimental results at selected potentials, plotted in the impedance plane, for an amorphous WO_3 film deposited at an O_2/Ar ratio of 0.44. The results for other potentials as well as for films deposited at other O_2/Ar ratios showed the same qualitative features, namely a depressed semicircle at high frequencies crossing over to a diffusion-like behaviour at lower frequencies. The depressed semicircle in the impedance plane at high frequencies (Fig. 2a) is ascribed to the

properties of the electrolyte/film interface. The effects of ion diffusion are visible at lower frequencies but the low frequency behaviour (Fig. 2b) is clearly different from the predictions of ordinary diffusion models [9]. This leads us to the realization that anomalous diffusion models [16] are necessary to interpret our results.

Figure 2 shows that the models described above result in very good fits of the experimental data with standard deviations of the fit never exceeding 0.06, and usually considerably smaller. In some cases a resistance, ascribed to parasitic side reactions in the electrochemical cell, had to be added in parallel to Z_{AD} in order to accurately describe the impedance at the lowest frequencies. This was necessary only in a range of low potentials below 1.5 V or 2 V vs. Li/Li^+ and this resistance was quite high, of the order of 30 to 100 k Ω .

Figure 3 shows the standard deviation of the fit of the AD1a and AD1b models to the experimental data, for the same sample as in figure 2. It is seen that the AD1b model is clearly superior at potentials above 1.8 V, while the AD1a model gives a slightly better fit at potentials lower than 1.8 V. Similar results were obtained for films deposited at the other O_2/Ar ratios. This result exhibits an interesting correlation to the reversibility of the charge capacity, i.e. the amount of Li ions that can be intercalated into the electrochromic WO_3 film at a certain potential. In order to characterize the charge capacity of our films we replot the data in figure 1 in the capacitance plane. Figure 4 shows a plot of imaginary capacitance as a function of real capacitance. The plot exhibits an approximately semicircular arc in the low frequency region. A measure of the so-called chemical capacitance [25], dQ/dU , was obtained by a low frequency extrapolation of this arc to the real capacitance axis. The obtained charge capacity is expressed as the number of ions (or equivalently charge compensating electrons from the back contact) inserted into the film per unit potential and formula unit of WO_3 . Figure 5a shows charge capacity obtained from impedance spectra starting at 3.2 V then sequentially taken down to 2.1 V (“intercalation”) and subsequently up to 3.2 V again

(“deintercalation”). It is seen that the charge capacity was not significantly changed after impedance measurements in the region between 3.2 V and 2.1 V, implying that ion insertion/extraction is highly reversible in this range.

However, the charge capacity decreased after impedance measurements below 2 V. Figure 5b shows data similar to those in figure 5a, but now taken in the lower potential region from 2.2 V to 1.6 V and then back again. We observe a significant decrease of the charge capacity during deintercalation (ion extraction) after the impedance measurements at 1.6 V. In fact, the charge capacity already starts to decrease at 1.8 V for the intercalation (ion insertion) data. Recent results on ageing of electrochromic WO₃ films [22,23] show that some of the inserted Li ions are irreversibly trapped in the film at low potentials around 1.5 V. Hence it seems that the transition from AD1b to AD1a behaviour of the impedance spectra is concurrent with the transition from reversible to irreversible ion insertion. This is line with the physics behind the two models, namely that the number of diffusing particles is conserved in the AD1b theory but not in the AD1a theory.

We now discuss the fitting parameters of the circuit in figure 1 and focus on the physics of ion diffusion in WO₃ thin films. The charge transfer resistance was mostly in the range of 10 to 100 Ω , slowly increasing with potential. At around 3 V vs. Li/Li⁺ it exhibited a steeper increase with potential, approaching values in the k Ω range. Figure 6 shows the effective diffusion coefficient and the anomalous diffusion exponent as a function of potential. The diffusion coefficient exhibits values in the range from 10⁻⁹ to 10⁻¹¹ cm²/s, with the films deposited at lower O₂/Ar ratios having the higher values. The D_{eff} depends strongly on the applied potential and exhibits the largest values at potentials lower than 1.5 V and higher than 3 V. Our diffusion coefficients are significantly higher than those obtained in earlier work [26] for sputtered films deposited at an even higher O₂/Ar ratio of 1.25. This is in line with the dependence of D_{eff} on O₂/Ar ratio observed in fig. 6a. Tungsten oxide films have also been deposited using various other methods under different conditions and

this invariably influences their properties. Earlier determinations of the diffusion coefficient show a quite high degree of scatter and were mainly carried out in the potential region between 2 and 3 V vs. Li/Li⁺. Despite the variety of deposition conditions, film structures and analysis methods, diffusion coefficients in the 10⁻¹⁰ cm²/s to 10⁻¹² cm²/s ranges were often reported [9,27-30], while somewhat higher values were found for a film produced by dip coating from a colloidal solution [31]. In general, our results are consistent with earlier works. Figure 6b shows that the anomalous diffusion exponent, n , also depends on the potential and exhibits values in the range 0.1 to 0.4. Also in this case the film deposited at a low O₂/Ar ratio exhibits values significantly higher than the other films. The exponent is in many cases quite close to that of a resistive value ($n=0$) which indicates that the ordinary diffusion model would be a fair approximation to the measured impedance response, although significantly inferior to the anomalous diffusion models employed here.

5. Conclusion

In conclusion, we have performed impedance spectroscopy on electrochromic amorphous WO₃ thin films in a wide potential range and under conditions of ion intercalation and deintercalation. We show that the impedance spectra are in excellent agreement with anomalous diffusion theories. The crossover from the AD1b model at high potentials to the AD1a model at low potentials is concurrent with the crossover from reversible to irreversible ion intercalation in the films. This is significant for physical understanding since in the AD1a model the number of diffusing ions is not conserved and a certain fraction is trapped in the film. The AD1b model can be interpreted as due to ion hopping processes exhibiting a fractal dynamics. We find that fractional diffusion models are essential for the understanding of the dynamics of ion insertion into WO₃ as well as ion diffusion in the film. For our films, potential dependent diffusion coefficients in the range from 10⁻⁹ to 10⁻¹¹ cm²/s were obtained, with the films deposited at lower O₂/Ar ratios having the higher values. The anomalous diffusion exponent, n , depends also on potential and exhibits values in the range 0.1 to

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Fig. 1. (a) Generalized Randles circuit used to model impedance spectra. The circuit contains an electrolyte resistance, R_{ohm} , an interfacial charge transfer resistance, R_{ct} , a double layer constant phase element CPE_{dl} , and a distributed anomalous diffusion element Z_{AD} . (b) The anomalous diffusion element is a transmission line with impedances χ_m and ζ_m . (c) In the case of AD1a model, χ_m is a resistance and ζ_m is a constant phase element (CPE), while in the AD1b model χ_m is a CPE and ζ_m denotes the impedance of a capacitor. The CPE's are denoted by q_m .

Fig. 2. Imaginary impedance vs. real impedance for an amorphous WO_3 film prepared at an oxygen/argon ratio of 0.44 and measured in a Li^+ containing electrolyte. Spectra were measured in the frequency range 10 mHz to 100 kHz at the potentials vs. Li/Li^+ given in the figure. Some frequencies are also marked in the figure. Measured data are denoted by symbols and full lines

denote fits by anomalous diffusion models as described in the main text. Symbols are the same in both (a) and (b)

Fig. 3. Standard deviation of fits of two anomalous diffusion models to experimental impedance data for an amorphous WO_3 film prepared at an oxygen/argon ratio of 0.44, as a function of potential vs. Li/Li^+ .

Fig. 4. Imaginary capacitance vs. real capacitance for a WO_3 film prepared at an oxygen/argon ratio of 0.44, measured in a Li^+ containing electrolyte. Spectra were measured in the frequency range 10 mHz to 100 kHz at the potentials vs. Li/Li^+ given in the figure. Some frequencies are also marked in the figure.

Fig. 5. Charge capacity of inserted Li ions/electrons per unit potential and formula unit, dq/dU , as a function of potential vs. Li/Li^+ , for a WO_3 film prepared at an oxygen/argon ratio of 0.70 and measured in a Li^+ containing electrolyte. Spectra were taken starting at the highest potential, then lowering the potential in steps to gradually intercalate more ions. Subsequently the potential was increased in steps to the initial value to deintercalate ions. Potential ranges were 3.2 to 2.1 V vs. Li/Li^+ (a) and 2.2 to 1.6 V vs. Li/Li^+ (b). Data were extracted from a low frequency extrapolation in complex capacitance plots similar to fig. 4.

Fig. 6. (a) Effective diffusion coefficient of Li^+ ions and (b) anomalous diffusion exponent as a function of potential vs. Li/Li^+ , for amorphous WO_3 films prepared at the oxygen/argon ratios given in the inset.

Figure Captions

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