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Anomalous diffusion of ions in electrochromic tungsten oxide films

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ABSTRACT

Amorphous tungsten oxide thin films were deposited by sputtering at different O_2/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} cm^2/s, and anomalous diffusion exponents in the range 0.1 to 0.4, with the films deposited at lower O_2/Ar ratios exhibiting the higher values.

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].

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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 In_2O_3:Sn (ITO; 10 Ω/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/cm^2. The RBS compositional analysis did not show significant departures from the stoichiometric WO_3 composition, but previous measurements with Elastic Recoil Detection Analysis [20] gave evidence for a slightly substoichiometric composition of films produced at the lowest O_2/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 $LiClO_4$ 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/cm^2. 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 Seconary Ion Mass Spectroscopy (SIMS) [23] have conclusively shown that Li ions are intercalated electrochemically into WO_3 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

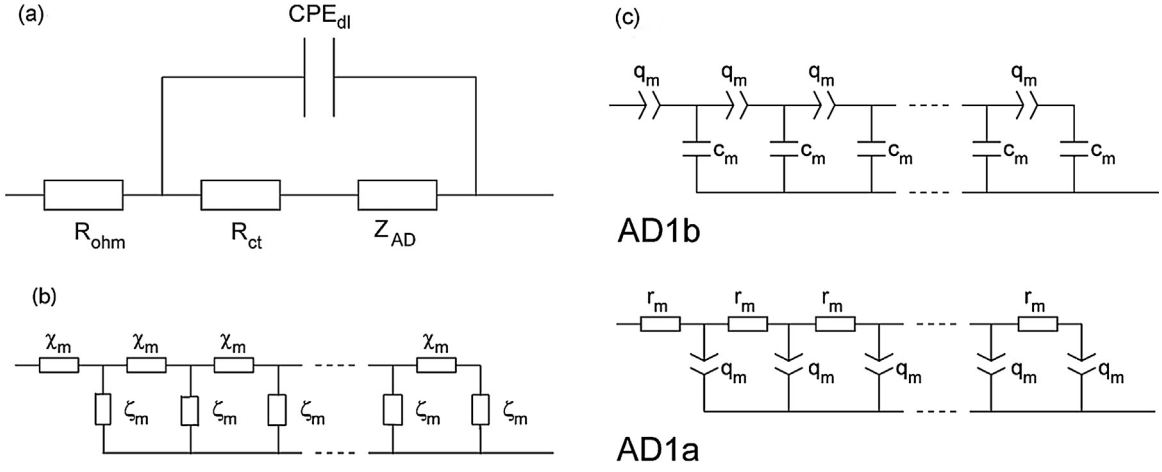

Fig. 1. (a) Generalized Randles circuit used to model impedance spectra. The circuit contains an electrolyte resistance, R_{ohm}, an interfacial charge transfer resistance, R_{ct}, a double layer constant phase element CPE_{dl}, and a distributed anomalous diffusion element Z_{AD}. (b) The anomalous 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.