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ION TRANSPORT IN POROUS Sn OXIDE FILMS: CYCLIC VOLTAMMOGRAMS INTERPRETED IN TERMS OF A FRACTAL DIMENSION

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Sn oxide films, made by reactive r.f. magnetron sputtering, were studied in a Li^+ -conducting electrolyte. Cyclic voltammograms taken at different sweep rates were interpreted in terms of a unique structural parameter related to the fractal dimension of a self-affine surface relief. Copyright © 1996 Elsevier Science Ltd.

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THIS COMMUNICATION reports on cyclic voltammetry probing Li^+ intercalation/deintercalation in porous Sn oxide films. Data taken at different sweep rates are interpreted in terms of a fractal dimension [1] consistent with a surface relief.

Solid state ionic devices such as batteries, sensors and electrochromic elements rely for their function on joint insertion/extraction of ions and electrons in a host material, often being an oxide [2, 3]. The ion dynamics limits the device performance in many cases, which points at the importance of, firstly, establishing powerful techniques to elucidate the fundamental insertion/extraction processes and, secondly, applying these techniques in the development of host materials with superior microtopologies. Below we employ two novel methods [4, 5] for obtaining a unique constitutive parameter characterizing the host material from cyclic voltammetry data. The parameter may be associated with a fractal dimension d_f . Atomic Force Microscopy (AFM) gave evidence in favor of d_f being representative of the relief for a self-affine surface of the film.

Sn oxide films were made by reactive r.f. magnetron sputtering in a versatile turbo molecular pumped vacuum deposition unit with a background pressure below 10^{-7} Torr. Sputtering took place from a 5-cm-diameter Sn (99.999%) target in Ar (99.998%) mixed with O_2 (99.998%). The power was 300 W, delivered at 13.56 MHz. The gases were introduced via mass-flow-controlled regulators keeping the total pressure during sputtering at 40 mTorr. Films were deposited onto unheated glass plates precoated with transparent

and conducting $\text{In}_2\text{O}_3 : \text{Sn}$ (known as ITO) layers having a resistance/square of 16Ω . The target-substrate distance was 15 cm. The target was inclined so that the sputtered species reached the substrate at an off-normal angle of $\sim 35^\circ$. Film uniformity was assured by substrate rotation. Presputtering was carried out in two steps: in pure Ar for 5–10 min in order to clean the target from oxide, and for 10 min with the desired sputtering parameters with the purpose of establishing stable deposition conditions.

The films to be analyzed below were made in an O_2/Ar volume ratio of 0.076 ± 0.005 and had a thickness, determined by surface profilometry, of 335 ± 12 nm. The deposition rate was 14.9 ± 0.5 nm min^{-1} . The resistance/square, measured with a four-point probe, lay in the $\text{G}\Omega$ range; this indicates a composition essentially without oxygen vacancies or other dopants [6], i.e. a film with a nominal SnO_2 stoichiometry.

Surface reliefs of as-deposited films were obtained by AFM using a NanoScope III instrument with an etched silicon cantilever having a tip radius of 10 nm and 35° apex angle. Data were taken in ambient air with a contact force of about 10^{-7} N. Scans were made over areas from 1000×1000 nm to 100×100 nm with a resolution of 512×512 pixels. Figure 1 illustrates a typical AFM image. Rounded protrusions with a lateral extent of 50–100 nm are apparent. The fractal dimension for the image, calculated by a box-counting method [7], was 2.3 ± 0.1 for boxes ranging from ~ 7 nm to 250 nm in linear size.

It is known [8–10] that suitably prepared Sn

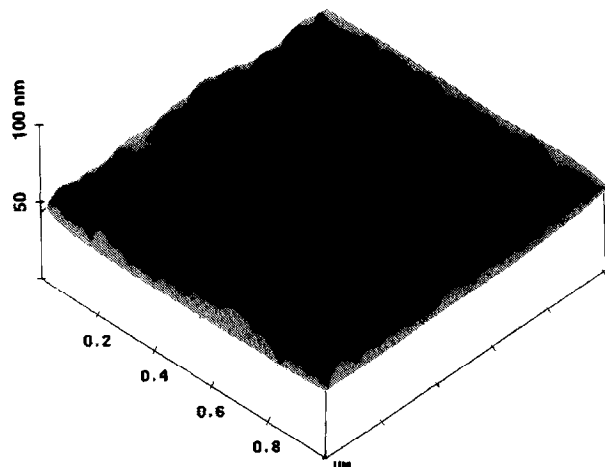


Fig. 1. AFM image of an as-sputtered Sn oxide film.

oxide films are porous enough to sustain reversible intercalation/deintercalation of small ions. The pertinent quasipotactic reactions have not been investigated in detail, but experience [3] from many electrochromic oxides leads us to surmise that lithiation takes place, schematically, by



with e^- denoting electrons.

We studied the insertion/extraction dynamics by cyclic voltammetry with the Sn oxide film, backed by ITO-coated glass, immersed in an electrolyte of 1 M LiClO_4 in propylene carbonate (PC). A standard three-electrode arrangement [11] was used with the Sn oxide serving as working electrode and Li foils as counter and reference electrodes. The experiment

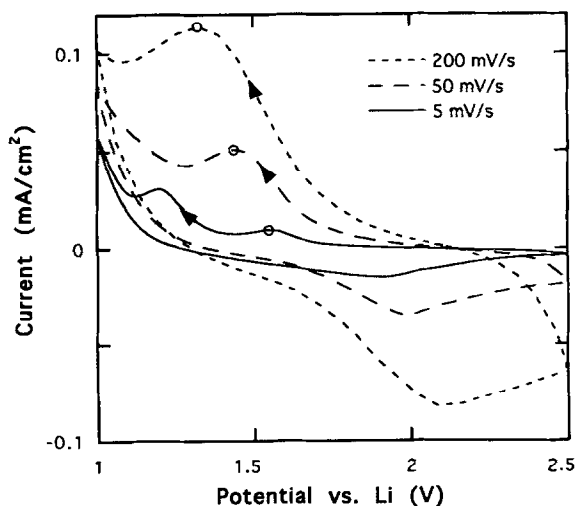


Fig. 2. Cyclic voltammograms for an Sn oxide film in $\text{LiClO}_4 + \text{PC}$. Data were taken at different voltage sweep rates. Arrows denote sweep direction. Circles indicate values of i_{peak} .

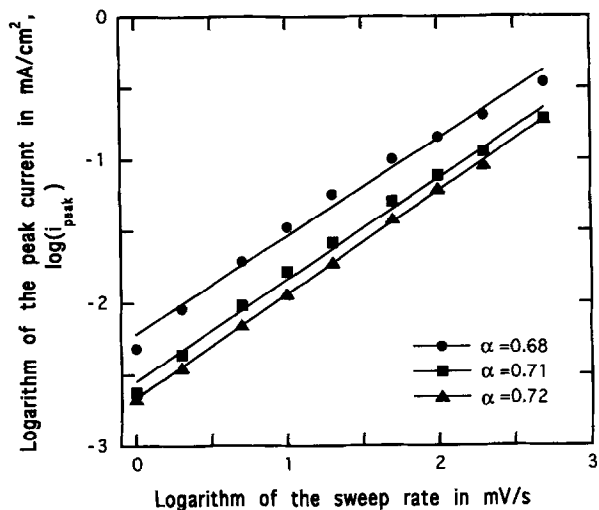


Fig. 3. $\log(i_{\text{peak}})$ vs $\log \nu$ for three Sn oxide films in $\text{LiClO}_4 + \text{PC}$. The straight lines, drawn as least-square fits to the individual data points, yield the shown values of α .

employed a Solartron 1286 electrochemical interface and was conducted in an Ar^- atmosphere containing less than 5 ppm of water (dew point below -64°C).

Figure 2 shows typical cyclic voltammograms taken between 1 and 2.5 V vs Li at three magnitudes of the voltage sweep rate ν . Unambiguous current peaks appear at intermediate voltages; they are particularly prominent in the cathodic sweep direction and at high rates (indicated by circles in Fig. 2). The rate-dependent shifts of the current peaks are those expected from a nonzero electrical resistance in the electrolyte and film. Additional cathodic peaks show up at $\nu < 50 \text{ mV s}^{-1}$.

Figure 3 illustrates the current at the (main) cathodic peak, denoted i_{peak} , as a function of ν for $1 < \nu < 500 \text{ mV s}^{-1}$. A relation

$$i_{\text{peak}} \propto \nu^\alpha \quad (2)$$

is clearly obeyed with

$$\alpha = 0.70 \pm 0.02 \quad (3)$$

for the studied samples. The applicability of relation (2) is the key result of our present work and proves that important features of the reversible charge transfer can be described in terms of a unique parameter α .

The same parameter can also be obtained using another electrochemical method – the Laplace transform method [5] – on each of the voltammograms recorded on the SnO_2 samples. When a function $\xi(s)$, which contains the Laplace transform of the current and the Laplace transform of a function of the potential, is plotted vs the Laplace transform variable s in a log–log diagram, the parameter α is obtained

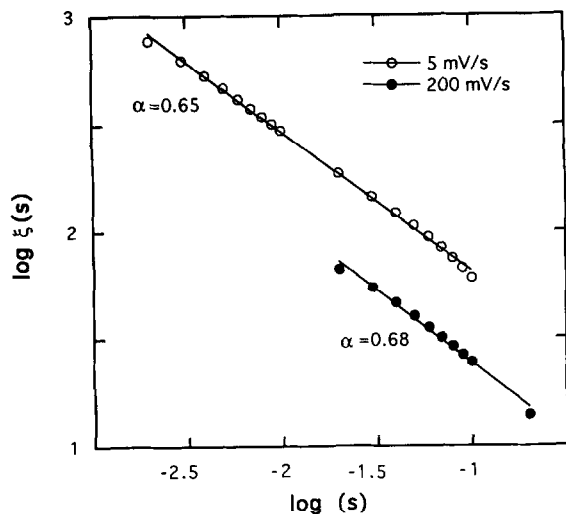


Fig. 4. Function ξ plotted vs Laplace transform variable s for a Sn oxide film in LiClO_4 + propylene carbonate. The transform was applied to voltammograms recorded at sweep rates between 2 and 500 mV s^{-1} , and the calculated ξ is shown for two of them. Values of α were extracted from linear fits to the individual data points. The basis of the Laplace transform method is given in [5].

from the linear fit to the data [5]. The result of the Laplace transform method, when used on two different voltammograms recorded on one of the samples, is shown in Fig. 4. Applying this method to each of the voltammograms recorded on the SnO_2 samples, we obtain an α of 0.67 ± 0.04 , in good agreement with the result from the peak-current method.

The theoretical basis for relation (2) and for the Laplace transform method was explored recently [4, 5]. A reversible electrochemical reaction was assumed, so that the Nernst equation applies, and currents were taken to be limited by ion diffusion towards the electrode surface. With these provisos, it is possible to express surface concentrations of the ionic species as a function of a Riemann–Liouville transform of the order $-\alpha$ [12], and diffusion to a fractal surface is governed by

$$\alpha = (d_f - 1)/2. \quad (4)$$

In our experiment the current is most likely controlled by Li diffusion inside the electrode, i.e. away from the electrode surface. Using the empirical α extracted from the peak-current and the Laplace transform method, we find $d_f = 2.35 \pm 0.09$, which is

in excellent agreement with the fractal dimension obtained from the surface relief using AFM and box-counting. The peak-current method senses distances at the surface ranging from $\sim 2 \text{ nm}$ to $\sim 150 \text{ nm}$. This is readily obtained by calculating the width of the diffusion layer [12] at the time when the peak-current is reached for the different sweep-rates in Fig. 3. In conclusion, the surface-size ranges investigated in AFM and in voltammetry are overlapping.

Summarizing, we have investigated sputtered Sn oxide films by cyclic voltammetry at different sweep rates and by AFM. Important features of the charge/extraction can be understood in terms of a unique parameter that can be related to the surface topography of the film. Our work gives insights into the materials characteristics governing the dynamics of solid state ionic devices.

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