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DETERMINATION OF ELECTRONIC STRUCTURE BY IMPEDANCE
SPECTROSCOPY

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Abstract

We present a novel method, based on electrochemical intercalation and impedance spectroscopy, to determine the electronic density of states of disordered transition metal oxides. Specifically, we have determined the “electrochemical density of states” of tungsten and iridium oxide thin films over energy ranges as wide as 1 to 2 eV. Our experimental results show a number of qualitative features exhibited by state-of-the-art band structure computations. Differences in details are probably due to the disordered, porous and sometimes amorphous nature of our films. The results suggest that the impedance spectroscopy method can be used to obtain the density of states only if the conduction band states are localized. The electrochemical density of states is often smaller than the computed one due to kinetic effects, i.e. very slow relaxations of the charge carriers. Nevertheless, our sensitive method opens new vistas for studying the electronic structure of disordered materials.

1. Introduction

A detailed knowledge of the electronic structure of functional materials is a necessary prerequisite for understanding their physical properties. The electronic structure of crystalline materials has been studied in detail by density functional calculations [1], and by a variety of experimental probes. Especially, electron and X-ray spectroscopic methods have led to great advances in understanding the electronic structure of a large variety of elements and compounds [2,3]. However, computations for amorphous and disordered structures are demanding and at present limited to small clusters [4]. For amorphous and nano-crystalline materials, there exists a need for accurate experimental probes of the disorder-induced localized states close to the band edges, which are of prime importance for many physical properties [5,6].

It has recently been appreciated that various electrochemical techniques can be used to obtain the electronic density of states (DOS) of a number of intercalation compounds [7-9]. Ions and charge-balancing electrons are intercalated into the material under study by electrochemical techniques. The electrons enter previously unoccupied states above the Fermi level of the host material. Provided that the inserted ions have a negligible influence on the electronic structure of the material, the number of inserted electrons as a function of voltage will give a qualitative image of the conduction band DOS. For certain materials it is instead possible to extract ions and electrons and an image of the valence band can be obtained.

In this paper we report on the applicability of electrochemical impedance spectroscopy (EIS) to determine the electronic DOS of transition metal oxides used as electrochromic materials [10]. By this technique, information on the DOS can be obtained from the so called chemical capacitance [11], which often dominates the response at low frequencies. We have studied a number of electrochromic transition metal oxide thin films, produced by sputtering, as detailed in sect. 2. In sect. 3, we present novel results for the electrochemical DOS of tungsten and iridium oxide thin films over energy ranges of 1-2 eV, and compare with electronic structure computations for the crystalline oxides.

2. Experiments

Samples of tungsten oxide (WO_x), iridium oxide (IrO_x) and iridium-tantalum-oxide (IrTaO_x) were prepared using reactive DC magnetron sputtering onto $\text{In}_2\text{O}_3\text{:Sn}$ (ITO; 10 Ω /square) covered glass substrates. A multi target sputter system, based on a Balzers UTT400 unit, was used with 99.95 % pure metallic 5 cm diameter targets positioned 13 cm from the substrate. The deposition took place in a 99.995 % pure argon-oxygen atmosphere at about 20 mTorr in the case of tungsten oxide and 30 mTorr for the other oxides. The O_2/Ar flow ratio was 1 when depositing IrO_x films and 0.13 when depositing IrTaO_x films. For tungsten oxide three values were used, namely 0.16, 0.44 and 0.70 . The sputtering power was 200 W during deposition of WO_x and IrO_x . It was 100 W for the Ir target and 220 W for the Ta target during deposition of IrTaO_x . Film thicknesses were determined to be in the range 85 nm to 110 nm, using an Alpha Step profilometer. Additional structural characterization of the films was presented in recent papers [12,13]. The compositions of the as-deposited films were $\text{WO}_{3\pm 0.1}$, $\text{IrO}_{2.2}$ and $\text{IrTa}_{1.4}\text{O}_{5.6}$, as obtained from Rutherford Backscattering

Spectrometry and X-ray Photoelectron Spectroscopy. The densities were found to be in the range 5-6 g/cm³ for WO_x and approximately 3 g/cm³ for IrO_x and 6 g/cm³ for IrTaO_x. The WO_x films were X-ray amorphous, while a grain size of 3-4 nm was found for both types of iridium containing oxide films. It is evident that IrO_x has a very porous structure.

Electrochemical measurements were performed using a standard three-electrode setup with the film under study as working electrode, a platinum or lithium counter electrode, and an Ag/AgCl or Li/Li⁺ reference electrode, all submerged in electrolyte. The electrolytes used were 1M LiClO₄ in propylene carbonate or 0.1M H₂SO₄ for tungsten oxide, and 1 M propionic acid for the iridium containing oxides. Prior to the EIS studies, the IrO_x and IrTaO_x films were pre-treated using cyclic voltammetry (CV) until a stable response was obtained (~10 cycles), using an Ecochemie Autolab/GPES interface.

Impedance spectroscopy was performed using a Solartron 1260 frequency response analyzer together with a Solartron 1286 electrochemical interface. The spectra were recorded using a 10 mV amplitude ac potential between 1 MHz and 10 mHz with 10 points per decade. Random errors were minimized by integration over three cycles at each frequency. Spectra were recorded at different potentials after applying the potential for 900 s to 1800 s allowing the films to attain a steady state. The potential ranges were: 3.2V to 1V vs. Li in the case of Li⁺ intercalation into WO_x, 0.3V to -0.5V vs. Ag/AgCl for H⁺ intercalation into WO_x and -0.2V to 0.8V vs. Ag/AgCl for H⁺ intercalation into Ir-containing oxides.

3. Results

3.1 Experimental data

Figures 1 and 2 show examples of impedance spectra plotted in different representations. The complex capacitance of a WO_x film deposited at $\text{O}_2/\text{Ar}=0.16$ is shown in fig. 1 for different applied potentials vs. Li. It exhibits an approximate semicircle for frequencies below 10 Hz. As the potential is lowered and more and more Li is intercalated, the low frequency chemical capacitance exhibits a non-trivial variation with potential. Examination of the spectra in the impedance plane reveals that the response is more complicated than a depressed semicircle in the C-plane. Fig. 2 shows two impedance spectra for IrOx (a) and IrTaOx (b), one recorded at high potential and the other at low potential vs Ag/AgCl. The small semicircle between 50 Hz and 3 kHz has been identified as due to the charge transfer resistance and the double layer capacitance, whereas the feature above 3 kHz has been identified as an ohmic resistance, mainly from the electrolyte, and a frequency dependent capacitive component, which probably is related to the reference electrode. The low frequency behaviour exhibits deviations from a pure capacitance at low potentials; this feature is a result of a side reaction in the electrochemical cell, as discussed elsewhere [14]. Corresponding results for WO_x were qualitatively similar, although the side reaction effect was smaller and the electrolyte resistance was different for each electrolyte. Figure 2 illustrates a behaviour that is characteristic of electrochemical systems.

3.2 Equivalent circuit fitting

The data were analyzed by equivalent circuit modeling [15] using modifications of the Randles circuit to account for anomalous diffusion kinetics. In the model fits we used only frequencies in or below the range corresponding to the ohmic resistance (typically below 3 to 10 kHz), in order to avoid errors and artifacts due to instrumental response at high

frequencies. The best fit between model and experimental data was achieved by using the equivalent circuit shown in Fig. 3a. It contains an ohmic resistance, R_{ohm} , a charge transfer resistance, R_{ct} , a double layer capacitance C_{dl} , a distributed anomalous diffusion element [16], B_3 , and a side reaction resistance, R_{sr} . Addition of the side reaction resistor enabled improved fitting in the low frequency region, in particular at low bias potentials for the Ir-containing oxides. The B_3 element in the circuit can be visualized by a transmission line, as illustrated in Fig. 3b; its impedance is equal to [16]

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

where L is the film thickness. Two anomalous diffusion models denoted AD1a and AD1b [16] are of interest for the present study. For AD1a, χ_m is a resistance and ζ_m is a constant phase element (CPE), while in AD1b χ_m is a CPE and ζ_m denotes the impedance of a capacitor [16]. The impedance of a CPE can be written as

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

where n is the distributed CPE exponent, which is equal to zero for ordinary diffusion, and q_m the distributed CPE prefactor, which has the dimension $\{(\Omega/m)s^{-n}\}$. The models described above resulted in good fits of the experimental data with standard deviations never exceeding 0.06, and usually considerably smaller. In most cases the AD 1b model gave the best fits to the experimental spectra. However, the AD 1a model was better in the

case of Li intercalation into WO_x at potentials below 1.5 to 1.8 V vs. Li, where the intercalation process was found to be irreversible.

4. Discussion

In this section we discuss the determination of the DOS from impedance spectroscopy data. The DOS can be obtained from the so called chemical capacitance in the low frequency region. As shown by Bisquert [10], it can be written as

$$C_{ch} = e^2 \frac{dN}{dE}, \quad (3)$$

where dN/dE is the number of electrons inserted per unit energy. This quantity is called the electrochemical density of states (EDOS). By dividing with the number of metal atoms we obtain the EDOS per formula unit, dx/dE . The chemical capacitance is calculated from

$$C_{ch} = L / (i\omega\zeta_m), \quad (4)$$

for the AD 1b model, where the denominator in eq. (4) is the inverse of the capacitance per unit length. For the AD 1a model ζ_m is a frequency dependent CPE and we suggest to approximate $(\omega\zeta_m)$ by the amplitude of its imaginary part, $q_m \sin((1-n)\pi/2)$.

Figure 4 compares the measured EDOS of WO_x with state-of-the-art bandstructure computations for the monoclinic phase [7]. A problem with such a comparison is that it is

necessary to fix the theoretical conduction band edge on the electrochemical potential scale. This was done by shifting the theoretical curves along the energy axis in order to obtain best agreement with experiments. After this procedure, we observe good qualitative agreement for energies up to 1 eV from the edge of the conduction band (3.05 V vs. Li/Li⁺ and 0.1 V vs. Ag/AgCl). However the measured EDOS is lower than the computed DOS. Hence all electronic states cannot be probed by the intercalated species, because of very slow relaxations of the predominantly localized electrons. It is also seen that intercalation of protons leads to a higher EDOS than Li intercalation. This is expected since protons are smaller and should be able to penetrate the tungsten oxide more rapidly. The intercalation was reversible up to 1 to 1.2 eV from the band edge. In the case of Li intercalation, it was also possible to study the region of irreversible intercalation at higher energies (lower potentials), where the inserted ions/electrons cannot be extracted again. Here the AD1a model gave best fits to experimental spectra. This is expected since in this case the number of diffusing ions is not conserved [16] and the model should describe trapping processes [17]. In addition the measured EDOS departs from the theoretical calculation in this region. It is interesting that this departure occurs close to the mobility edge of amorphous WO_x [18]. Hence it seems that the existence of localized electronic states is a prerequisite for obtaining a good representation of the DOS of the material by impedance spectroscopy. Figure 4b also shows a curious feature observed during the first cycle of proton intercalation, namely that extra states show up at the band edge as the charge is extracted and these states persist in subsequent cycles. This points to changes in the film structure in the first intercalation cycle and indicates that proton and Li intercalation may lead to different material properties.

Figure 5 shows the measured EDOS for IrO_x (a) and IrTaO_x (b) together with a theoretical DOS of crystalline IrO₂ [19]. As shown in the figure, the Fermi level of IrO_x was used as a reference for the energy scale. The overall picture is much the same as in the case of WO_x. It can be seen that the EDOS is 30-50% of the theoretical DOS, but that it shows the same main features as the theoretical DOS with a peak slightly above the Fermi level of IrO₂ and a declining DOS for higher energies. This agreement is particularly good for IrTaO_x whereas the measured DOS of IrO_x shows less features. However, the data for the IrO_x film are more uncertain, being more affected by side reactions [14]. Also IrO_x exhibited a very porous disordered structure, which might affect the DOS.

5. Conclusions

We have shown that impedance spectroscopy is a versatile method for measuring the electrochemical density of states of transition metal oxide intercalation materials. We have studied the EDOS of amorphous tungsten, iridium and iridium-tantalum oxide thin films and shown that it is proportional to the theoretically computed electronic density of states. Quantitative discrepancies are attributed to the characteristic very slow relaxations of electronic charge carriers in these materials as well as to effects of disorder. Our method shows good qualitative agreement with theory, provided that the studied electronic states are localized. Further work is necessary on a number of issues such as the origin of anomalous diffusion, the effect of irreversible intercalation and the response in the case of extended states.

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Figure captions.

Fig. 1. Imaginary vs. real capacitance for tungsten oxide films intercalated with lithium at the shown potentials. A few frequency values are given for the uppermost set of data; they are also indicative of the order of magnitude of the frequency at corresponding points for the other potentials.

Fig. 2. Complex impedance plots at two potentials for IrOx (a) and IrTaOx (b). The insets show the high frequency region in detail. Some frequencies are indicated on each curve.

Fig. 3. (a) Equivalent circuit used for fitting experimental impedance spectra, containing ohmic resistance, R_{ohm} , double layer capacitance C_{dl} , charge transfer resistance, R_{ct} , an anomalous diffusion element, B_3 , and side reaction resistance, R_{sr} . (b) The anomalous diffusion element in a transmission line representation.

Fig. 4. Electrochemical density of states as a function of energy from the conduction band edge for tungsten oxide films intercalated with Li ions (a) and protons (b). Errors in the experimental points were mostly of the order of 1 % and always less than 3 %. The experimental data were fitted to the computed DOS of monoclinic WO_3 [7] by a small shift along the energy axis and multiplication with a constant as given in the figure.

Fig. 5. Electrochemical density of states during proton intercalation and deintercalation, for IrO_x (a) and IrTaO_x (b) films together with the theoretical DOS of IrO₂ calculated by Xu,

Jarlborg, and Freeman [19]. Errors in the experimental points were mostly lower than 0.5 % and always less than 3.5 %.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5