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Electrochemical measurements of the electronic density of states

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Abstract

We present a simple electrochemical method, called intercalation spectroscopy, to study the electronic density-of-states of intercalation materials. It is based on the realization that electrochemical quasi-steady state potential curves of a number of materials exhibit fine structure in good agreement with features in the density of electronic states. Different electrochemical techniques are able to give this information, but chronopotentiometry appears to have advantages from an experimental viewpoint. In this paper we compare the so called “electrochemical density-of-states” of amorphous and crystalline structures. We also address the limitations of intercalation spectroscopy due to kinetic effects, i.e. very slow relaxations of the charge carriers. Intercalation spectroscopy is in principle very sensitive, although in limited energy ranges, and is able to give information complementary to electron and X-ray spectroscopies for a number of materials.

1. Introduction

The electronic structure and electronic density of states (DOS) of crystalline and amorphous materials constitutes the basis for the description of their physical properties, including the electrical, optical and magnetic ones. In this paper we focus on transition metal compounds, especially those which can accommodate intercalated ions, for example protons and lithium ions. Experimental studies of the DOS by electron and X-ray spectroscopies have contributed greatly to our understanding of the electronic structure of these materials [1,2]. The increased capacity and versatility of ab initio density functional calculations [3] has also led to new developments in this field.

However, there exists a need for developing simple and widely accessible methods for studying the DOS close to the Fermi level as well as defect states in the band gap. To this end

electrochemical methods are of interest, especially for materials which are able to intercalate ionic species. When small ions such as protons or Li ions are intercalated into a material from an electrolyte, electrons must be inserted from the back contact to maintain charge neutrality. These electrons will enter into unoccupied electronic states and the Fermi level will shift upwards in energy as intercalation proceeds. Alternatively, extracting ions and charge-balancing electrons will lead to a downward shift of the Fermi energy. Provided that the rigid band approximation holds during the intercalation process, measuring the charge inserted or extracted will give an image of the electronic density of states [4-6]. The DOS in regions of 1 to 2 eV from the Fermi level can be measured by these so called intercalation spectroscopy [4] techniques, for example chronopotentiometry (CP) [7], Galvanostatic Intermittent Titration (GITT) [8] and electrochemical impedance spectroscopy (EIS) [7].

In this paper we briefly review and discuss some experimental aspects of intercalation spectroscopy. Experimental data from our previously published work serve as a basis for discussing three issues that have been largely neglected before. First, we compare amorphous, nanocrystalline and polycrystalline structures and discuss the information that can be obtained from intercalation spectroscopy in these cases. Secondly, we discuss the pro and contra of the three techniques CP, GITT and EIS. Thirdly, we address the important question of kinetic effects which may distort the DOS as measured by intercalation spectroscopy.

2. Experimental techniques

All electrochemical methods used in this work employ a three-electrode arrangement with the sample under investigation serving as working electrode (WE). The intercalation of monovalent cations M^+ with charge balancing electrons e^- into the WE material S may be represented, schematically, as

where x denotes the fraction of intercalated ion-electron pairs per formula unit of S. In intercalation spectroscopy the WE potential, U, is measured for an as wide as possible range of intercalation levels, x. The derivative $-dx/dU$ gives a normalized number of charges inserted per energy interval and is denoted the “electrochemical density of states” (EDOS). It is a measure of the number of electrons and ions inserted into the film per unit energy and can be directly compared to the computed electronic DOS.

In this paper we will present results from intercalation of Li^+ ions in different oxides. In this case metallic Li foils were used as counter- and reference electrodes in an electrolyte consisting of 1M LiClO_4 in propylene carbonate. When the WE is inserted into the electrolyte it attains an open circuit potential (OCP), which gives the position of the Fermi level of the WE relative to the Li/Li^+ potential of the reference electrode. More experimental details can be found in the works quoted below in this section.

The CP method to measure the EDOS was developed by Strömme et al. [4]. A constant current is applied between the working and counter electrodes and the WE potential is continuously measured, as ions and electrons are intercalated into the WE. It is necessary to use a very low constant current, of the order of $1 \mu\text{A}/\text{cm}^2$ [4], in order to be in a quasi-steady state situation. These measurements can be carried out relatively fast, depending on the magnitude of the applied current.

In the related GITT technique [8], ions and electrons are intercalated by applying a low constant current under a limited time period and the potential of the cell is recorded after it has been allowed to relax to its steady-state value. In the measurements discussed below, a current of $3.2 \mu\text{A}$ was applied for 100 s, and afterwards the cell was allowed to relax for 1000s [9]. This procedure was repeated until the composition interval of interest was covered. GITT generally gives more precise values of the steady-state potential at the expense of very time-consuming measurements, since dielectric materials exhibit very slow relaxation towards the steady-state potential.

In EIS, a sinusoidal signal superimposed on a constant voltage bias is applied to the WE and the complex impedance is measured for frequencies from the mHz to the high kHz ranges. Measurements discussed below used a 10 mV amplitude ac signal with frequencies from 10 mHz to 1 MHz [10]. This was done for a number of bias potentials between 3.2 V and 1 V vs. Li. The low-frequency asymptotic chemical capacitance gives information on the EDOS at the applied voltage bias, as noted by Bisquert [11].

3. Results and discussion

We have compared the measured EDOS to density functional calculations for a number of oxides, namely WO_3 [4,6], TiO_2 [4], V_2O_5 [12], CeO_2 [13] and IrO_2 [14], and found significant qualitative agreement. We have also lately studied some transparent metal oxides such as $\text{In}:\text{SnO}_2$ and $\text{Sb}:\text{SnO}_2$ [15], as well as some NiO based coatings. The case of WO_3 is

especially interesting, since it has been studied by the CP, GITT and EIS methods and in addition both crystalline and amorphous samples have been measured.

We now address the influence of the crystallinity of the coatings on the experimental results. Figure 1 shows the quasi-steady state potential as a function of Li/W ratio, x , for crystalline and amorphous WO_3 . The potential of the polycrystalline sample (grain size ~ 50 nm) exhibits three plateaus around $x \sim 0.05$, 0.3 and 1 , respectively [16]. The potential of the amorphous sample decreases smoothly as x increases, although one may note some broad structures in the curve. The nanocrystalline sample (grain size ~ 5 nm) [17] shows an intermediate behavior. The features are broader than for the polycrystalline sample, but the structure around $x \sim 0.3$ is close to one of the plateaus in the crystalline data. Figure 2 shows the EDOS of the three samples. The plateaus in the potential curves correspond to sharp peaks in the EDOS. These are most pronounced in the case of crystalline WO_3 , but it is seen that a similar behavior occurs for the nanocrystalline sample, although at somewhat different potentials. The nanocrystalline sample exhibited a lower OCP (3.03 V) than either of the polycrystalline (3.3 V) and amorphous (3.46 V) films. On the other hand, amorphous WO_3 displays a smooth EDOS curve without sharp peaks. The features in the curve are very similar to those of the computed DOS of monoclinic WO_3 , as shown before [4], and also illustrated below in figure 3.

The plateaus in the potential for crystalline WO_3 are related to phase transitions occurring during the intercalation process [16,18]. During Li intercalation the structure evolves from monoclinic to tetragonal to cubic and the first two plateaus coincide with transitions between these phases [18]. In the plateau region two phases coexist and ions are inserted into the low x phase, which then locally transforms to the high x phase. Hence the ions are inserted into energetically equivalent sites. This situation can be modeled by the lattice gas model (LGM) [19,20], where one assumes that each intercalated ion is exposed to a mean interaction potential, W , from its intercalated neighbors and that the electron energy does not vary significantly. The WE potential can be expressed as

$$U = E_0 + kT \ln \frac{1-x_r}{x_r} - Wx_r + V_{el} \quad (2)$$

The four terms on the right hand side are the ion site potential (E_0), the entropy associated with the intercalated ions, the ion-ion interactions and the potential of the inserted

electrons. In Eq. (3), k is Boltzmann's constant, and T the temperature. The ions are taken to occupy a fraction x_r of all available and energetically equivalent sites in the host.

It is realized that there is no simple way to obtain an EDOS from V_{el} for crystalline materials which show phase transitions during intercalation. First, the electronic and ionic parts in eq. (2) are not additive in $-dx/dU$. Secondly, the existence of different phases in different regions of the parameter x , even makes the concept of an EDOS meaningless.

In Figure 3 we compare the EDOS of amorphous WO_3 , as obtained by the CP [4], GITT [9] and EIS [10] techniques. The computed DOS of monoclinic WO_3 [4] is also shown for comparison. The zero of energy was put at the OCP of the material used as WE. The energy scale in the computations was adjusted in order to achieve a good fit of the most prominent peaks of the DOS to the CP experiments. It is seen that the EDOS obtained from CP shows almost the same structure as the computed DOS, although only half of the electronic states seem to have been populated during the CP experiment. This is because the inserted electrons did not have enough time to relax completely during this non-steady state experiment. In addition, the ions do not distribute uniformly in the coating but probably exhibit a gradient in concentration, due to slow kinetics of the process. On the other hand, the steady-state GITT experiment shows an EDOS of similar magnitude as the computed one, but without features that can be unambiguously identified in the computations. In this experiment full relaxation of the inserted charge carriers was ensured. However, the long duration of the experiment might have induced aging of the samples. In addition, small parasitic side reactions in the electrochemical cell would be more likely to affect a steady state experiment such as GITT. The EDOS curve for the EIS measurement is much below the other ones. It seems that significantly less charge is inserted during the EIS experiment. The reason for this is not known at present. Other capacitive processes, perhaps connected with the interfaces in the WE, might be superimposed on the chemical capacitance at low frequencies. However, the shape of the EDOS, apart from a multiplicative factor, is in good agreement with the computed DOS up to 1 eV from the band edge, as shown before [10]. At higher energies (lower potentials), the intercalation process is not reversible and the EIS experiment indicates reaction or trapping processes, probably the formation of Li compounds [10]. It is clear that the EDOS is not reliable in the presence of strong side reactions. The side reactions are probably of less importance in CP, because of slow diffusion of ions to the reaction/trapping sites.

Figure 4 shows another example of qualitative agreement between the experimental EDOS and computed DOS, namely for CeO_2 [13]. A puzzling result is that the EDOS

resembles not the total DOS of the lowest Ce 4f conduction band, but instead the DOS of an admixture of oxygen 2p states [13]. The reason for this is not known, but it should be noted that the inserted Li ions will most likely bind to oxygen ions in the material.

The relaxation towards the steady state has recently been explored by Montero et al. [15] by Li intercalation CP experiments on Sb-doped SnO_2 . Figure 5a shows potential vs. time for CP experiments carried out by using four different currents. The CP experiments were terminated after the same amount of charge was inserted into the sample, and subsequently the potentials were allowed to relax to equilibrium. It is seen that the same final potential was obtained in all cases, which indicates that this is really the correct steady-state potential. Applying a higher current allows to explore a wider potential region, but during a shorter time. Obviously the inserted charge per potential unit is higher the lower the current. It seems that the intercalation process at the highest current is sufficiently fast so that side reactions, expected to occur below 2 V vs. Li [15] are not significant.

We now take a further step and consider how the EDOS depends on the magnitude of the applied current. It is obvious that the EDOS will be lower at higher applied currents since the inserted charge is spread over a larger potential interval. However, will the shape of the EDOS be the same independent of the applied current? Figure 5b shows the inserted charge per potential unit for the four curves in figure 5a. It is seen that the shape of the EDOS pertaining to the three lowest currents are similar. An initial convex shape reminiscent of a free electron like DOS can be seen, but this crosses over to a parabolic or exponential shape below 3 V. For the highest current, charge insertion was so fast that the shape above 2.5 V could not be studied in detail. It is not known whether the rise below 2 V is a real feature of the EDOS or due to side reactions. Summing up, there appears to be a rather wide current window in the CP technique that gives reasonably similar results for the EDOS.

4. Conclusions

We have reviewed the use of electrochemical techniques to obtain information on the electronic DOS of intercalation materials. These methods are denoted intercalation spectroscopy and seem to work best for amorphous materials, although nanocrystalline ones have also been studied successfully [14,15]. However, phase transitions in a crystalline material during the intercalation process make the determination of the EDOS impossible. The chronopotentiometry technique offers a good compromise between experimental simplicity and charge insertion capacity. It has also been able to produce EDOS data in good

agreement with features of the theoretically computed DOS [4,12]. Slow relaxations of charge carriers to lower energy states might distort the measured EDOS and these effects should be studied in more detail in the future. It is suggested that intercalation spectroscopy will be useful for screening the EDOS of a large amount of materials in the laboratory, not only oxides, but also other non-metals, such as sulfides. Then interesting materials and specimen can be selected for further studies by other techniques, such as photoelectron or X-ray spectroscopies at synchrotron facilities.

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Figure captions

Fig. 1: Quasi-steady state potential (normalized to the potential of the Li electrode) as a function of Li/W ratio, x , in polycrystalline, nanocrystalline and amorphous WO_3 films. Experimental data were taken from ref. 4 and ref. 17.

Fig. 2: Electrochemical density of states, $-dx/dU$ as a function of potential (U) vs. the Li electrode, for the polycrystalline, nanocrystalline and amorphous WO_3 films in figure 1.

Fig. 3: Electrochemical density of states, $-dx/dU$ as a function of energy for amorphous WO_3 films, obtained by chronopotentiometry, Galvanstatic Intermittent Titration (GITT) and Impedance Spectroscopy (IS). The zero of energy was put at the experimental open circuit potentials of the films. The theoretically computed density of states of monoclinic WO_3 (from ref. 4) is shown for comparison.

Fig. 4: Electrochemical density of states, $-dx/dU$ as a function of energy for CeO_2 films (ref. 13), obtained by chronopotentiometry (dashed line), together with the computed O 2p density of states (ref. 13) in the lowest empty band in CeO_2 (full line).

Fig. 5: (a) Potential as a function of time during chronopotentiometry experiments using the currents given in the figure, and subsequent relaxation to equilibrium, for Sb:SnO_2 thin films. Data were obtained from ref. 15. (b) Derivative of inserted charge with respect to potential for the same films as in figure (a).

Fig. 1

Fig. 2

Fig 3

Fig 4

Fig 5