Properties of the capacitance and carriers diffusivity in nanostructured electrode materials

Juan Bisquert

Departament de Ciències Experimentals
Universitat Jaume I
12080 Castelló

There is currently a great deal of interest in heterogeneous devices formed by a nanostructured electrode material filled with a conductive phase (electrolyte or polymer).

A crucial feature for the applications in photovoltaics and batteries is the ability of these systems to incorporate a large number of carriers (either ionic or electronic) homogeneously in the nanostructure. The electrode potential is related directly to the Fermi level or chemical potential in the nanostructure. The variation of the electrode potential is therefore connected to the density of states in the material. Examples are shown in Figs. 1 and 2.

In order to understand the electrochemical properties of these systems it is essential to characterize the main electrochemical techniques response in the presence of typical distributions of states. Here we discuss the main aspects of two central techniques, electrochemical impedance spectroscopy [1-4] and cyclic voltammetry [5], arising from a distribution of localized sites in the materials. We describe properties of carriers incorporation in terms of the measured capacitance. We distinguish the capacitance component related to accumulation of carriers in the nanostructured material and the components arising from interfacial charging.

The capacitive response is related to thermodynamics and electrostatic features of the system. It is also important to recognize the kinetic aspects involved in the electrochemical techniques, related to carrier transport and reactivity. We consider the diffusion of carriers, which is usually a dominant aspect in applications such as Li ion batteries and dye-sensitized solar cells. The examples shown in Figs. 1 and 2 suggest that the diffusion of carriers in these types of materials is a complex process that departs heavily from a simple fickean diffusion. The carriers hop between localized states with widely different energies, implying a distribution of hopping times. Moreover some carriers become trapped at deep states.

We discuss the electrochemical impedance spectra related to diffusion of carriers in different distributions of localized sites, like those shown in Fig. 1 and 2. We discuss the variation of the diffusion coefficient with respect to the electrode potential in the framework of the two-state model shown in Fig. 1.We demonstrate the origin of anomalous diffusion patterns observed in disordered materials in terms of an exponential distribution of states shown in Fig. 2.

A general conclusion is the enormous disparity of electrochemical responses that can be found in nanostructured heterogeneous electrochemical devices. We demonstrate a strong correlation between the capacitance and the diffusivity: both properties come ultimately from the density of states in the nanostructured material. We suggest that this correlation provides a key for characterizing these materials and devices.

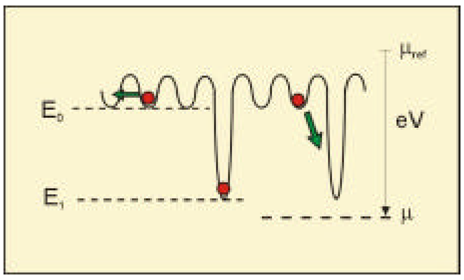

Fig. 1. Scheme of a two-state model for an intercalation system. The chemical potential of ions μ is related to the electrode potential *V* and determines the occupancy both of deep states E_1 and shallow states E_0. In a lattice gas μ follows Fermi-Dirac statistics so that states lying bellow μ are essentially fully occupied. The arrows indicate the processes of solid state ion diffusion through shallow states, and ion trapping.

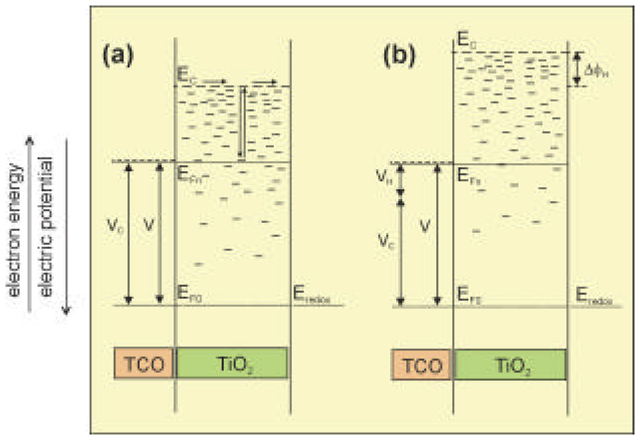

Fig. 2. Scheme of electronic states in a TiO_2 nanoporous electrode permeated with a redox electrolyte. (a) The scheme shows two classes of electronic states in the TiO_2: extended states (conduction band) of energy E_c and an exponential distribution of bandgap localized states. The Fermi level E_{Fn} is controlled by the potential V in the TCO and determines the occupancy of both the extended and localized states. (b) Under partial band unpinning by charging at the Helmholtz layer, the cell potential is $V = V_C + V_H$, where V_C indicates the true displacement of E_{Fn} with respect to E_c.

References

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