Comment on "Diffusion Impedance and Space Charge Capacitance in the Nanoporous Dye-Sensitized Electrochemical Solar Cell" and "Electronic Transport in Dye-Sensitized Nanoporous TiO$_2$ Solar Cells−Comparison of Electrolyte and Solid-State Devices"

Juan Bisquert*

*Departament de Ciències Experimentals, Universitat Jaume I, 12080 Castelló, Spain*

In the recent literature of nanoporous TiO$_2$ electrodes permeated with a liquid electrolyte and dye-sensitized solar cells, there has been identified a large capacitance that increases exponentially with the negative bias potential. Normally, the capacitances measured in electrochemical systems relate the inhomogeneous charge distribution in some interface to the electric field between these charges. However, this capacitive mechanism will not easily lead to an exponential capacitance. Recent papers[1,2] have emphasized the interpretation of the exponential capacitance in terms of a diffusion capacitance, by adopting an analogy of nanoporous TiO$_2$ electrodes with solid-state pn-junctions. But recent work[3−5] indicates a simpler interpretation of the capacitance. We view a nanostructured TiO$_2$ film as a container that accumulates electrons, raising their chemical potential. Similarly, a silicon p-doped "film" in the pn-junction accumulates minority electrons when forward biased, although the latter system has an ohmic contact at the other side from the junction, so it cannot accumulate electrons (minority carriers) homogeneously. Here, we compare the impedance measurements for nanoporous TiO$_2$ electrodes permeated with a liquid electrolyte and solid-state pn-junctions, emphasizing the idea of a "chemical potential capacitance" or, more simply, chemical capacitance, as defined in the literature.[6,7] We argue that this capacitance can be defined locally in the film volume, that it is not diffusional in origin, and neither related to charge separation in the electrostatic capacitor at the junction.

The electron concentration in a semiconductor film that is biased negatively at the left contact is represented schematically in Figure 1.[3] The electron density at the left contact is

$$n_s = n_0 \exp(-eV/k_B T) \quad (1)$$

where n_0 is the equilibrium concentration, e is the positive electron charge and $k_B T$ is the thermal energy. The factor $-eV$ is the local electrochemical potential of electrons at the contact, with respect to the equilibrium value. Equation 1 is a statement involving two conditions: (i) the classical statistics of electrons in the film and (ii) the assumption of a reversible contact to electrons (one that has zero impedance), so that V, the bias electrical potential, relates to chemical potential of electrons in TiO$_2$ as $-eV = \Delta\mu_n = \mu_n - \mu_{n0}$, with respect to the equilibrium value. Condition (ii) means that the quasi-Fermi level of electrons is continuous at the contact between the film and the phase at the left, under current flow. This holds both for the contact between the quasi-neutral p-doped region with the space-

* To whom correspondence should be addressed. E-mail: bisquert@uji.es.
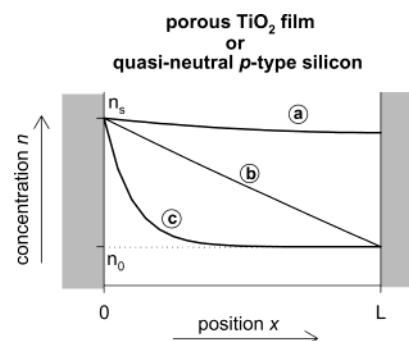
Figure 1. Schematic representation of the carrier distribution in a semiconductor film biased negatively at the left contact with blocking boundary (a) and absorbing boundary (b) at the right contact. Curve (c) corresponds to the conditions of high recombination.

charge region and for the nanoporous TiO$_2$ contact with the transparent conducting substrate.

Let us revise the diffusion−recombination impedance for the systems shown in Figure 1.[3] For the nanoporous TiO$_2$ film, the blocking (reflecting) boundary condition applies at the right contact, and the impedance of diffusion coupled with recombination is given by[3]

$$Z = \left(\frac{R_d R_k}{1 + i\omega/\omega_k}\right)^{1/2} \coth[(\omega_k/\omega_d)^{1/2}(1 + i\omega/\omega_k)^{1/2}] \quad (2)$$

where R_d is the diffusion resistance, R_k is the recombination resistance, $\omega_d = D_n/L^2$ is the characteristic frequency of diffusion in a finite layer (D_n being the electron diffusion coefficient), and ω_k is the rate constant for recombination.

The conditions of low recombination can be defined as those at which the diffusion length, L_n, is much larger than the film size, L. In these conditions, for the nanoporous TiO$_2$ film, the electrochemical potential of the left contact (imposed by the bias potential) extends almost homogeneously through the film, by an overall increase of the chemical potential of electrons in the bulk film, as shown in curve a of Figure 1. In the conditions of low recombination, $R_d \ll R_k$, eq 3 reduces to the expression

$$Z = \frac{1}{3}R_d + \frac{R_k}{1 + i\omega/\omega_k} \quad (3)$$

An example of this impedance behavior, measured in nanostructured TiO$_2$ electrodes in solution, is shown in Figure 2a. Because in the conditions of low recombination the gradient of concentration is very small (curve a in Figure 1), the 45° line of diffusion is a minor feature at high frequencies. The impedance is largely dominated by the reaction arc, the second term in eq 3. The feature in question is the meaning of the capacitance appearing in this arc, given by eq 8, below, in the case of very low recombination.

On another hand, if we are in conditions of large recombination, defined either by $L_n \ll L$ or $R_k \ll R_d$, the electron distribution will be like in curve c of Figure 1, and the general impedance of eq 2 becomes the Gerischer impedance
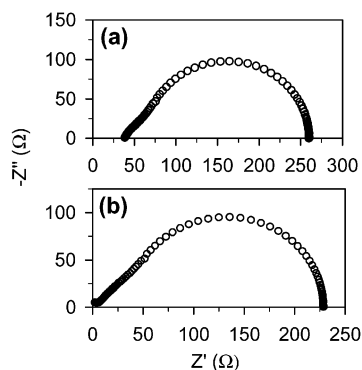
$$Z = \left(\frac{R_d R_k}{1 + i\omega/\omega_k}\right)^{1/2} \quad (4)$$

This case is shown in Figure 2b. In contrast with eq 3, where
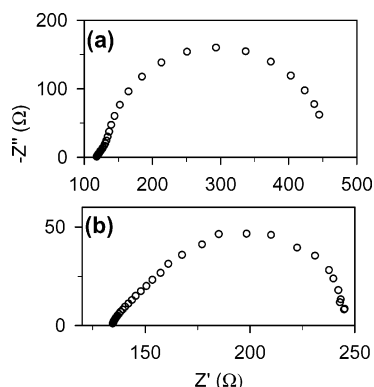
Figure 2. Experimental impedance spectra of UV illuminated nanoporous TiO_2 film (20 nm diameter anatase particles) in pH 2 solution with 10% ethanol. Bias potential is (a) −0.450 and (b) −0.100 V vs Ag/AgCl.

Figure 3. Experimental impedance spectrum of a silicon pn-junction. (a) As measured. (b) After removal of the contributions of series resistance and space-charge capacitance.

diffusion and reaction are basically separated, in eq 4 the two processes are mixed.

Let us consider the other system, the quasi-neutral silicon p-doped region in the pn-junction, having an ohmic contact at the right. In this case the impedance is[3]

$$Z = \left(\frac{R_d R_k}{1 + i\omega/\omega_k}\right)^{1/2} \tanh[(\omega_k/\omega_d)^{1/2}(1 + i\omega/\omega_k)^{1/2}] \quad (5)$$

In the conditions of low recombination, the ohmic contact extracts all of the excess carriers and the carrier distribution in the film is straight, as shown in curve b of Figure 1. Then eq 5 can be simplified as

$$Z = R_d(i\omega/\omega_d)^{-1/2} \tanh[(i\omega/\omega_d)^{1/2}] \quad (6)$$

On the other hand, in the conditions of high recombination, the concentration profile is that shown in curve c of Figure 1. Obviously, the boundary condition at the right contact is completelly irrelevant, and accordingly, the general expression of the impedance, eq 5, reduces to the Gerisher impedance, eq 4, like in the nanoporous film.

The similarity is confirmed by the impedance measurement of a silicon pn-junction shown in Figure 3 (see ref 8). In Figure 3a, the impedance spectrum is shown as measured. The high frequency 45° line of diffusion is distorted by the effect of the junction capacitance. When we remove the series resistance and the junction capacitance, the spectra shown in Figure 3b shows an excellent example of the Gerischer impedance, like Figure 2b. So in the conditions of high recombination, the two systems

are completely analogous concerning electron distribution and impedance response.

We analyze the interpretation of the capacitance observed in nanoporous TiO_2 electrodes, that increases exponentially with the negative bias potential. In curve a of Figure 1, by neglecting the small gradient, we can write the concentration of electrons in the film, from eq 1, as

$$n = n_0 \exp(-eV/k_B T) \quad (7)$$

and so the capacitance per unit electrode area will be

$$C = -Le\frac{dn}{dV} = Le^2\frac{dn}{d\mu_n} = Le^2\frac{n}{k_B T} \quad (8)$$

It can be checked readily[3] that the capacitive component of the diffusion impedance in eq 4 is given by eq 8. It is seen that the capacitance of eq 8, depending exponentially on the bias, as confirmed experimentally,[1,2,4] is related to the statistics of electrons in the material. The Boltzmann distribution function for conduction band electrons is incorporated in eq 8. Other distribution functions, for example due to the presence of band gap electronic states, will provide a different dependence of the capacitance on the bias potential.[5] Thus, the expression $C = Le^2 (dn/d\mu_n)$ is the chemical capacitance of electrons,[6] which is one component of the electrochemical capacitance.[7]

Traditionally, the capacitance of eq 8 was observed in solid-state pn-junctions at forward bias, as commented below, and was termed a diffusion capacitance. However, in pn-junctions, the physical origin of the capacitance is the same as in the nanostructured TiO_2 film: an increase of chemical potential of electronic species, minority carriers in this case. The total capacitance is found integrating eq 8.

By the different boundary conditions in Figure 1, it is observed that, if recombination is low, the TiO_2 film can contain electrons homogeneously, whereas the p-material loses them through the ohmic contact. This contrast follows from the fact that one system is a nanoscaled composite of two materials, and the other one a homogeneous material. The implications of this difference for the photovoltaic mechanisms in both systems will be discussed elsewhere.

In conclusion, the capacitance measured in nanostructured TiO_2 films permeated with electrolyte by impedance methods is a property of the whole nanoporous film, it is obtained by integrating the local values of the chemical capacitance, it is proportional to the film thickness, L, and it cannot be properly understood as a junction capacity related to the contact of the film with the conducting substrate. Rather than interpreting the capacitance in nanoporous TiO_2 electrodes as a consequence of diffusion,[1,2] we think it is much more fruitful for discussions of photovoltaic principles to go the other way around, taking the chemical capacitance observed in nanoporous TiO_2 as a primary thermodynamic quantity as defined in the literature.[6,7] In fact, this chemical capacitance concept establishes that the locus of energy storage by charge accumulation is not generally linked to the locus of electrical field variation.

References and Notes

(1) Schwarzburg, K.; Willig, F. *J. Phys. Chem. B* **2003**, *107*, 3552−3555.

(2) Kron, G.; Egerter, T.; Werner, J. H.; Rau, W. *J. Phys. Chem. B* **2003**, *107*, 3556−3564.

(3) Bisquert, J. *J. Phys. Chem. B* **2002**, *106*, 325.

(4) Fabregat-Santiago, F.; Garcia-Belmonte, G.; Bisquert, J.; Zaban, A.; Salvador, P. *J. Phys. Chem. B* **2002**, *106*, 334.

(5) Fabregat-Santiago, F.; Mora-Seró, I.; Garcia-Belmonte, G.; Bisquert, J. *J. Phys. Chem. B* **2003**, *107*, 758.

(6) Jamnik, J.; Maier, J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1668.

(7) Büttiker, M.; Thomas, H.; Prêtre, A. *Phys. Lett. A* **1993**, *180*, 364.

(8) Bisquert, J.; Garcia-Belmonte, G. *Electron. Lett.* **1997**, *33*, 900.