Chemical capacitance of nanostructured semiconductors: its origin and significance for nanocomposite solar cells

Juan Bisquert*

Departament de Ciències Experimentals, Universitat Jaume I, 12080 Castelló, Spain.
E-mail: bisquert@uji.es; Fax: +34 964728066; Tel: +34 964728064

Received 8th September 2003, Accepted 6th November 2003

First published as an Advance Article on the web 14th November 2003

The capacitance measured in dye-sensitised nanocrystalline TiO$_2$ solar cells (DSSC) is interpreted in terms of a chemical capacitance, which is found to be a crucial feature for describing the dynamic operation of solar cells based on nanoscaled materials.

Interpenetrated networks of nanoscaled materials provide the opportunity to construct efficient solar cells from low purity materials and versatile fabrication processes. Instead on relying on long diffusion length in high purity crystals, the nanocomposite solar cells base their ability to convert photon energy to electricity on fast conversion of the photoexcitation to energetic carriers spatially separated in distinct nanoscaled phases, which enables their extraction.

In this paper we discuss the general principles of operation of these solar cells. We start from the thermodynamic model of chemical capacitance, and we show its special role in the dynamic model of the solar cell in terms of equivalent circuits for small modulated perturbation. We argue that the concept of chemical capacitance is of critical importance for nanostructured semiconductor solar cells, because it describes the fundamental mechanism whereby photogenerated carriers store chemical capacitance, and we show its special role in the dynamic operation of solar cells based on nanoscaled materials.

The DSSC$^1$ is so far the most efficient nanocomposite heterogeneous solar cell. In DSSC, the carriers transferring the chemical energy created in a photoexcited dye are electrons in nanocrystalline TiO$_2$, and redox species in a liquid electrolyte. The capacitance of DSSCs can be determined in several ways: electrochemical impedance spectroscopy (EIS),$^2$ cyclic voltammetry,$^5$ or integrating the current at differential voltage steps,$^6$ and provides important information on the density of states (DOS) and the electron density.

Normally, the concept of a capacitance relates to the textbook notion of an electrostatic geometric capacitance, determined by the electrical field between two metal plates with equal amounts of opposite charges. But this description is valid only insofar as the excess charge induced by the potential difference is confined to a very small region of the surface of the plates. Especially for mesoscopic systems, this is far from being generally true. In general, the change of electrochemical potential of electron reservoirs connected through leads to the mesoscopic plates, causes both an accommodation of the field by excess charges, and a variation of the Fermi level position with respect to the conduction band in the plates. Consequently, the more general electrochemical capacitance has been defined for small conductors connected to macroscopic reservoirs.$^7$

The basic result is that the DOS contributes a factor to the capacitance given by

\[ C_{\text{DOS}} = \frac{e^2 dN}{dE} \]  

(1)

where \( e \) is the absolute elementary charge and \( dN/dE \) is the total DOS of the mesoscopic plates.$^7$ When \( dN/dE \) is very large, eqn. (1) can be neglected with respect to the geometric electrostatic capacitance, as in macroscopic metal plate capacitors.

This idea can be applied readily to the DSSC configuration, as indicated in Fig. 1. Here, the two plates forming the capacitor are the whole TiO$_2$ nanostructure connected to transparent conducting oxide (TCO), and the whole electrolyte connected to Pt electrode, as indicated in the scheme at the bottom of Fig. 1. When the electrochemical potential of electrons, \( \mu_n \), is varied at the TCO side (by applying a voltage \( dV = -d\mu_n/e \) at the substrate) the subsequent electrical field is not located at the contact between the extended plates, because it is shielded at the TCO/TiO$_2$ contact,$^8,9$ as indicated by the lower conduction band edge of TiO$_2$, \( E_c \), being stationary in Fig. 1 (band unpinning is neglected here). Thus the basic notion of the capacitor does not hold. In fact the modification of the electrochemical potential at the substrate produces a change of the chemical potential of electrons in the TiO$_2$ nanostructure, \( d\mu_n \), with associated variation of both free electron density, \( d\text{ne} \), and localized electron density in band gap states, \( d\text{nl} \). In this case the electrochemical capacitance is dominated by a chemical capacitance, \( C_{\mu_n} \), related only to the

---

**Fig. 1** Electron energy diagram illustrating the behaviour of a nanocrystalline TiO$_2$ electrode (shown in the bottom scheme) when a variation \( dV \) of the electrochemical potential of electrons \( \mu_n \) (Fermi level) is applied, assuming that conduction band energy \( E_c \) remains stationary with respect to the redox level, \( E_{\text{redox}} \). The voltage variation is absorbed at the TCO/TiO$_2$ electrolyte interface. Inside the TiO$_2$ nanostructure, the Fermi level is displaced towards the conduction band, \( i.e. \), the chemical potential of electrons varies, \( d\mu_n \), what causes a charge of occupancy both of conduction band, \( d\text{ne} \), and trapped electrons in localized levels, \( d\text{nl} \) (shaded region of the bandgap).
variation of the electron chemical potential in the TiO$_2$ “plate” of the capacitor. In conclusion the sytem of Fig. 1 is a macroscopic chemical capacitor constituted by mesoscopic units.

Another, independent but equivalent formulation of the chemical capacitance is obtained from general thermodynamic considerations that define the capacitor as an ideal element that stores energy by virtue of a generalized displacement. If the volume element stores chemical energy due to a thermodynamic displacement, the chemical capacitance per unit volume is

$$C_p = e^2 \frac{\partial N_i}{\partial \mu_i}$$  \hspace{1cm} (2)

This is indeed another version of eqn. (1), but here the chemical capacitance is defined locally, in a small volume element, and in this interpretation the capacitance reflects the capability of a system to accept or release additional carriers with density $N_i$ due to a change in their chemical potential, $\mu_i$. From eqn. (2), in the case of an ideal mixture for which the chemical potential of the $i$th component is $\mu_i = \mu_i^0 + k_B T \ln N_i$, where $k_B$ is Boltzmann’s constant and $T$ the temperature, we get

$$C_{p(i)} = e^2 \frac{N_i}{k_B T}$$  \hspace{1cm} (3)

In this case energy is stored reversibly in the chemical capacitor as a change in entropy.

In the same way, using the Boltzmann distribution function for conduction band electrons,

$$n_i = N_e e^{(\mu_i - E)/k_B T}$$  \hspace{1cm} (4)

where $N_e$ is the effective density of conduction band states, the expression

$$C_{p(b)} = e^2 \frac{n_i}{k_B T}$$  \hspace{1cm} (5)

is obtained from eqn. (2). The total chemical capacitance of the system in Fig. 1, is given by the integral of eqn. (5) throughout the volume of the nanostructured film.

Considering the variation of both free and localized electrons indicated in Fig. 1 we obtain for the chemical capacitance of electrons in the DSSC

$$C_{\mu} = e^2 \frac{\partial (n_i + m_i)}{\partial \mu_i} = C_{p(b)} + C_{p(trap)}$$  \hspace{1cm} (6)

where

$$C_{p(trap)} = e^2 \frac{\partial m_i}{\partial \mu_i} = e^2 g(\mu_i)$$  \hspace{1cm} (7)

Here $g(E)$ is the density of localized states in the bandgap, at the energy $E$, as in eqn. (1). For the exponential distribution with tailing parameter $T_c$ (with $\alpha = T/T_c$)

$$g(E) = \frac{N_i}{k_B T_c} \exp[(E - E_c)/k_B T_c]$$  \hspace{1cm} (8)

the chemical capacitance in eqn. (7) can be expressed as

$$C_{p(trap)} = e^2 \frac{2N_i}{k_B T} \exp[\alpha(\mu_i - E_c)/k_B T]$$  \hspace{1cm} (9)

In conclusion, eqns. (5) and (9) show that the chemical capacitance in nanostructured TiO$_2$ is characterized by an exponential dependence on the bias potential. The electrochemical capacitance has been determined experimentally many times in nanostructured semiconductors and DSSCs, see e.g. refs. 3,5, and the exponential dependence is normally found. However, the ideal statistics of eqn. (5), with a slope $(e/ k_B T)^{-1} = 0.026$ V decade$^{-1}$ for $(d \ln C/dV)$ $^{-1}$, is not observed. The experimental results of about $(d \ln C/dV)$ $^{-1}$ = 0.100 V decade$^{-1}$ have been interpreted in terms of the trapped electrons in the exponential distribution described in eqn. (8). Which greatly exceeds the number density of free electrons in the conduction band.

As an example, in Fig. 2(a) we show the measurement of the capacitance of nanostructured TiO$_2$ electrodes in aqueous solution at pH 3, in conditions in which charge transfer to the electrolyte is very low. By using a model fitting, the ohmic potential drop can be removed in order to extract the variation of capacitance with the Fermi level position with respect to the conduction band. The results, shown in Fig. 2(b), reveal a chemical capacitance dominated by the exponential distribution of bandgap states as in eqn. (9), with a value of $\alpha = 0.25$. This interpretation of $C_f(V)$ is confirmed by other techniques such as a stepping charge-extraction method.

The expressions in eqns. (3) and (5) for a dilute species are quite familiar in solid-state electrochemistry. For semiconductors, the meaning of the capacitance in eqn. (5) as a charge storage element is clearly recognized by Sah who denoted it the electron charge storage capacitance.

On another hand, many semiconductor device books call eqn. (5) the diffusion capacitance (we have also used eventually this denomination in the past). The reason for this is indicated in the scheme of Fig. 3. When two adjacent volume elements are at a different chemical potential value, a diffusion process follows; this is an irreversible loss that attempts to equalize the charge in the chemical capacitors. Therefore, the diffusion process always requires the chemical capacitors, and these indeed appear in the well known equivalent circuit for diffusion (11,16,17) (the transmission line composed of the repetition of the arrangement in Fig. 3). But the converse is not true. While the extended chemical capacitor does indeed

![Fig. 2](image)

(a) Chemical capacitance of a 2.6 μm thick film of anatase TiO$_2$ nanoparticles (12 nm radius) in aqueous solution (pH 3) determined from cyclic voltammetry at scan rate $s = 0.2$ V s$^{-1}$. (b) The capacitance as obtained from the measured current ($C_f = I/(dV/dt) = I/s$), as a function of potential (vs Ag/AgCl reference electrode), and model fitting. The curved region at less cathodic potentials is due to a deep monoelectron surface state that is neglected in the model. (b) Chemical capacitance vs. electron Fermi level, after subtraction of the ohmic drop $IR$ in the potential axis in (a).
for electrons and holes, \( f \) changed significantly. Therefore sunlight irradiation, with generation of carriers \( \text{e} \) and destruction of conduction band electrons \( \text{e}^{-} \), causes the separation of quasi-Fermi levels \( \text{e}^{-} \) from the phase of high to the phase of low Fermi level. The upper line of the equivalent circuit for a small transient or periodic perturbation of the light intensity. The transverse elements represent the three main processes occurring in the solar cell: A photocurrent generator \( \text{i}_{\text{ph}} \), which is indicated in units \( \text{e}^{-} \), and \( \text{e}^{+} \) do represent transport currents, but the rates of creation and destruction of conduction band electrons.

The first term in eqn. (13) can be recognized as a capacitive current \( (\mathcal{I} = \mathcal{C} \mathcal{dV}/\mathcal{dt}) \). The capacitance \( \mathcal{C} \) for unit volume is obviously the chemical capacitance, \( \mathcal{C}_{\text{ch}} \), given in eqn. (5). For the solar cell operation it must also be possible to convert the chemical energy to electrical power. This process of “charge separation” has been discussed elsewhere in terms of selective contacts to the absorber. \(^{20}\) This is indicated in Fig. 5 for DSSC. The local circuit obtained in Fig. 4(c) for the absorber material, is combined with the appropriate contacts to form a solar cell. Note that each wire unites one side of the absorber (i.e. either of the carriers with separated Fermi levels) to one and only one metal electrode. The overall asymmetric configuration of the circuit, with the different lines of

\[
\frac{\mathcal{d}p_{\text{n}}}{\mathcal{d}t} = \frac{\text{g} - \rho_{\text{n}}}{\tau} \quad (11)
\]

We linearize eqn. (4) and obtain the relationship

\[
\rho_{\text{n}} = -\frac{\text{e}}{k_{\text{B}} T} \phi_{\text{n}} \quad (12)
\]

Multiplying eqn. (11) by \( \text{e} \) and substituting eqn. (12), we obtain

\[
ne^{2} \frac{\mathcal{d}p_{\text{n}}}{k_{\text{B}} T \mathcal{d}t} + eq + \frac{ne^{2}}{k_{\text{B}} T} \phi_{\text{n}} = 0 \quad (13)
\]

The absorption of sunlight, Fig. 4(b), has the effect of exciting a homogeneous slab of p-doped silicon crystal as indicated in Fig. 4. We choose this example because it contains no internal interfaces, so there are no possible electrostatic capacitors in the bulk of this system (indeed, there are no electrical field variations, except if global space charge is formed, which can be ignored in this model), and the effect of the chemical capacitance becomes unmistakable.

The absorption of sunlight, Fig. 4(b), has the effect of increasing the concentration of electrons in the conduction band with respect to the thermal equilibrium situation, Fig. 4(a). The concentration of holes in the valence band is not changed significantly. Therefore sunlight irradiation, with generation rate \( G \), causes the separation of the quasi-Fermi levels for electrons and holes \( \phi_{\text{e}} \) and \( \phi_{\text{h}} \), that are indicated in units of electrical potential \( \phi_{\text{e}} = -\mu_{\text{e}}/e \), Fig. 4(b). The electron density \( n \) is governed by the conservation equation,

\[
\frac{\mathcal{d}n}{\mathcal{d}t} = G - \frac{n}{\tau} \quad (10)
\]

where \( \tau \) is the lifetime.

We analyse the behavior of this system under a small perturbation of some physical variable. Let \( n \), \( \phi_{\text{n}} \) and \( G \) denote the steady state values, and \( \rho_{\text{n}} \), \( \phi_{\text{n}} \) and \( g \) the corresponding small perturbation values, so that the concentration is \( n + \rho_{\text{n}}(t) \), and the quasi-Fermi level is \( \phi_{\text{n}} + \phi_{\text{n}}(t) \). Since the steady-state values are time-independent, it follows from eqn. (10) that

\[
\frac{\mathcal{d}\rho_{\text{n}}}{\mathcal{d}t} = \frac{g - \rho_{\text{n}}}{\tau} \quad (11)
\]
selective contacts, converts the excess, photo-induced charge in the chemical capacitor to an output (photo)voltage and (photo)current.

With the insight obtained from the equivalent circuit model, we can appreciate that the macroscopic chemical capacitor of Fig. 1 incorporates also the selective contacts, so that it converts excess chemical energy of electrons in the TiO₂ nanoparticles (with respect to electrons in redox ions), to the electrochemical potential difference of carriers in outer leads. One can conclude that the capacitor shown in Fig. 1 is indeed the central structure of the solar cell.

Returning to Fig. 4(c) we can discuss the different processes involved in photon energy conversion. The complete structure of the solar cell is an electrochemical capacitor shorted by two elements: The current generator (excitation process) transfers charge from one plate to the other increasing the electrochemical potential difference. In DSSC this is realized by the dye molecules absorbed in the TiO₂ surface. And a leakage, recombination resistance, tends to reduce the electrochemical potential difference. Both the current generator and the leakage resistance for radiative recombination correspond to the same physical process occurring in inverse directions in time. In practice, recombination occurs through parallel radiationless pathways of lower resistance. Preferentially the leakage between the plates should be reduced, but it cannot be removed beyond the radiative recombination limit. A major strategy for improving the efficiency of nanocomposite solar cells is the treatment of the interface between nanoscaled components for increasing the recombination resistance, while maintaining fast separation of the excitation created by light.

We remark also that the leakage element provides the electronic connectivity between plates that is required for achieving the thermodynamic equilibrium in the dark, with equal Fermi levels in the two plates (at $V_{sc} = 0$), regardless of kinetics.

It is often argued that a diffusion process of the separate carriers is responsible for the photovoltaic effect. However, it is clear that diffusion is a purely irreversible process that cannot bring to bear a free energy gain. This paradox is resolved when we note that diffusion is important only for charge equalization into one plate of the macroscopic chemical capacitor. So diffusion is not a component of the fundamental structure of the solar cell shown in Fig. 4(c), but it allows to make this structure spatially extended, as indicated in Fig. 5. This is an important point for harvesting a substantial amount of incident photons.

We note also that the diode characteristic of solar cells is usually attributed to a diffusion process, following the model of Shockley for the p-n junction. However, the crucial effect governing the diode characteristic is the recombination of the injected carriers, and not their diffusion. Indeed, the diode characteristic is obtained directly from the leaky capacitor model of Fig. 4. The leakage current increases exponentially with increasing voltage, as follows from the expression $I_{rec} = k_I T e^{e V/e^2}$ and eqn. (4).

We remark also that the leakage element provides the electronic connectivity between plates that is required for achieving the thermodynamic equilibrium in the dark, with equal Fermi levels in the two plates (at $V_{sc} = 0$), regardless of kinetics. In conclusion, we argued that the fundamental structure of a solar cell is a leaky electrochemical capacitor. The solar cell is composed of two plates that maintain carriers with different electrochemical potentials (Figs. 1 and 5). Excitation is a charging of the electrochemical capacitor. Charge separation relies on a good connectivity into each of the macroscopic plates. Recombination is a leakage between the plates that should be minimized but cannot be suppressed. The electrochemical capacitor automatically describes the fundamental feature of selectivity of contacts in a solar cell.

These conclusions for DSSCs can be probably extended to other nanocomposite photovoltaic converters such as the organic solar cells consisting on a blend of conjugated polymers and fullerene molecules. Indeed, the concept of the chemical capacitor enables to formulate quantitative models for solar cell characterization by small perturbation techniques, and this will be shown more extensively in subsequent publications.

Acknowledgements

This work was supported by Fundación Caixa Castelló under project P11B2002-39.

References

27 M. A. Green, Physica E, 2002, 14, 11.