Capacitance probe of the electron displacement in a dye sensitised solar cell by an intermodulation technique : a quantitative model.

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For a dye-sensitised photo electrochemical cell (DSSC) SnO_2 / TiO_2 (nanocrystalline) / redox electrolyte /Pt/ SnO_2, it is well admitted that electrons injected from the excited state of the dye are diffusing through the TiO_2 nanostructure. As a consequence, the potential difference between the TiO_2 surface and the rear electrical contact essentially takes place at the SnO_2/TiO_2 junction. Impedance measurements show that doped SnO_2 is depleted at the SnO_2/TiO_2 interface in the potential range U= 0 (short circuit) to V_{oc} (open circuit). The corresponding space-charge differential capacitance C_d is found to present a Mott-Schottky behaviour, with a potential barrier maximum at U=0 and minimum at $U=V_{oc}$. For usual DSSC, C_d can be measured in the kHz range. Under illumination, electron concentration at the SnO_2/TiO_2 interface is defined by its Quasi-Fermi level (QFL), lined up with the Fermi level of SnO_2. When modulating the applied potential U at a frequency f_2 much lower than the C_d sampling frequency f_1, the capacitance C_d is modulated *via* the changes induced in the QFL by the time-dependent processes implied in the electron displacement in the TiO_2 structure. The so-called *intermodulation technique* consists of applying a composite sinusoidal signal $\Delta Uf_1 + \Delta Uf_2$ to the DSSC, with $f_1 \gg f_2$. The quadrature component of the *ac* total current is detected at the frequency f_1 by a Lock-In amplifier. Under certain conditions, the output signal is proportional to the C_d capacitance with a residual modulation at f_2. The f_2 component is then determined by a Frequency Response Analyser, typically in the range $f_1/10 > f_2 > f_1/10^5$ [1,2].

Dealing with capacitance, the charge-potential Q(U) characteristic is relevant to define the state of the electrochemical system. At any potential U, the ratio Q/U is defined as the integral capacitance C_{int}. The time-dependence of the displacement current I_d is $I_d = dQ/dt$. When superimposing a sinusoidal signal at $\omega_1 = 2\pi f_1$ to the *dc* potential U_o, the component of the current I_d at f_1 is :

$$I_{f1} = [U_o(dC_{int}/dU) + C_{int}(U_o)].j\omega_1.\Delta Uf_1$$

where the term in brackets is the differential capacitance C_d. In the case of a composite signal $\Delta Uf_1 + \Delta Uf_2$, it was demonstrated [2] that :

$$I_{f1f2} = [U_o(d^2C_{int}/d^2U) + 2(dC_{int}/dU_o)].j\omega_1.\Delta Uf_1.\Delta Uf_2$$

where I_{f1f2} represents the modulation at the frequency f_2 of the displacement current measured at f_1. The response of C_{int} to a potential perturbation is expressed as the sum of two terms, the first one is time-independent, only potential dependent, the second one is time-dependent. The transfer function experienced by the inter modulation technique is written as :

$$\Delta C_{f1}(f_2)/\Delta U(f_2) = \{\Delta C_{f1}/\Delta U\}_U + \{\Delta C_{f1}(f_2)/\Delta U\}_t$$

with

$$\{\Delta C_{f1}/\Delta U\}_U = [U_o(d^2C_{int}/d^2U) + 2(dC_{int}/dU_o)]$$

For DSSC, a quantitative expression for C_{int} is obtained when considering the space-charge formed at the SnO_2/TiO_2 interface. It allows the frequency independent term to be calculated. It is expressed as :

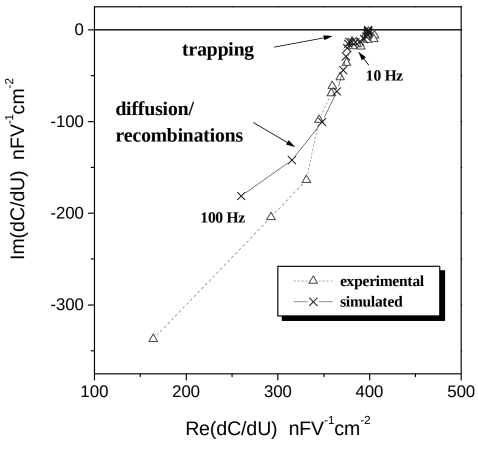
$$\{\Delta C_{f1}/\Delta U\}_U = -(q\varepsilon\varepsilon_o N/8)^{0.5}.(U-U_{fb})^{-1.5}$$

where q is the elementary charge, $\varepsilon\varepsilon_o$ and N are the dielectric permittivity and carrier density of SnO_2. Ufb is the flatband potential with respect to the SnO_2/TiO_2 interface. The frequency dependent term $\{\Delta C_{f1}(f_2)/\Delta U\}_t$ is calculated using expressions developed for IMPS [3]. It is formally expressed as

$$\{\Delta C_{f1}(f_2)/\Delta U\}_t = A.\mathrm{th}\sqrt{z} / (\sqrt{z} + B.\mathrm{th}\sqrt{z})$$

where the complex argument z depends on the processes taken into account (diffusion, recombinations, trapping). Capacitance being proportional to the surface area, this new transfer function allows to determine the actual TiO_2 surface coverage of the SnO_2 substrate. If normalized with respect to the geometric surface area, the measured (real or complex) quantity is expressed in $nF\ V^{-1}\ cm^{-2}$ units.

As a first example, in the dark, in the absence of any current, the response is a real constant. As a second example, an experimental Nyquist diagram recorded under illumination is given in the figure with comparison to the simulated curve according to the above model. The well separated low frequency loop is attributed to electron trapping-detrapping effects. The high frequency loop is related to diffusion-recombination processes.



<u>Fig.1:</u> Comparison between experimental and simulated Nyquist diagrams for a DSSC cell using a solid PEO-based electrolyte (Diffusion coefficient = 3.10^{-4} $cm^2.s^{-1}$; N = 2.10^{20} cm^{-3}; trapping rate constant= 50 s^{-1}; surface area = 0.3 cm^2).

References
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