

Coupling between electron displacement and the interfacial capacitance at the nanocrystalline TiO₂/electrolyte interface.

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Electrochemical interfaces are commonly characterised by analysing their linear electrical response to small perturbations in terms of electrochemical impedance. Such interfaces are defined both by the presence of ionic and/or electronic space charge regions and the presence of faradaic processes. The latter ones give rise to surface reactions involving charge transfer and transport in the electrolyte and eventually in the electrode bulk. The contribution of the overall interfacial charge (displacement currents) is represented by an interfacial capacitance C_i . Within the traditional picture, C_i is linked in parallel with the faradaic impedance (charge transfer reactions), assuming the superposition principle. From classical electrochemical impedance spectroscopy (EIS) measurements, it is not possible to check whether C_i is frequency independent or not as soon as Faradaic processes are taking place.

To overcome this difficulty, a new experimental approach has been recently developed in our laboratory, based on an intermodulation technique [1]. The basic idea was to follow the frequency modulation of the interfacial capacitance measured at a relatively high frequency $F = \omega/2$ (e.g. 1kHz) induced by a faradaic or a photoelectrochemical process excited in a lower frequency range (below 100 Hz). The response of the double layer is analysed as the derivative of the capacitance with respect to the perturbing signal, $dC/dE(\omega)$ for a potential perturbation, $dC/dI(\omega)$ for a light flux perturbation at the frequency $f = \omega/2$. The experimental set-up needs a lock-in amplifier operating at frequency F (EG&G 7265) coupled with a multichannel frequency response analyser (Solartron 1254) allowing to get the *complex* derivative of the capacitance and the usual *ac* electrochemical or photocurrent response. For instance, for the anodic dissolution of iron, the double layer capacitance was demonstrated to be frequency-dependent, may be due to the relaxation of surface intermediate coverage. In this presentation, this intermodulation technique is tentatively applied to the case of a dye-sensitised nanocrystalline TiO₂ photocell under illumination.

Our investigations were performed on a two-terminal cell with the configuration :

SnO₂:F / TiO₂ / N3dye / 0.1M LiI + 0.01M I₂ + PC / Pt / SnO₂:F

where PC stands for propylene carbonate. Preliminary EIS measurements showed that in the kHz range the impedance response is that of the SnO₂:F / TiO₂ interface. At 1kHz, a Mott-Schottky plot was obtained, representative of the band bending in the doped SnO₂ substrate and providing useful information on the energy scheme of the photoelectrode. A band edge shift was evidenced in the recombination region and the series resistance was found to vary significantly with potential. Figure 1 shows the typical profile in the complex plane of the measured signals.

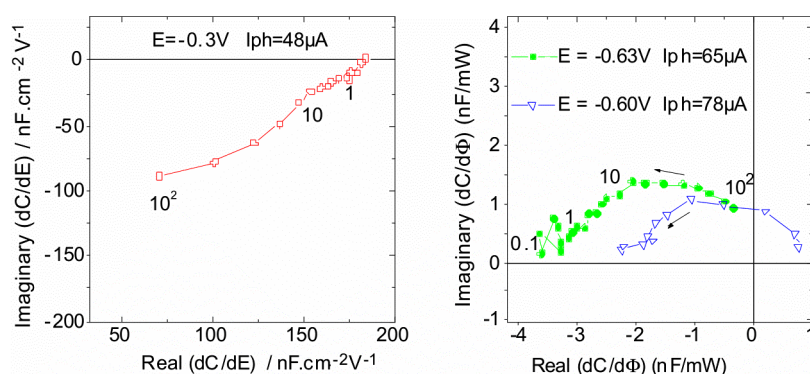


Fig.1 : Typical examples of the modulated capacitance depicted in the complex plane obtained with potential modulation (left) and light flux modulation (right) respectively.

These preliminary diagrams have been analysed by assuming all the potential modulation applied at the SnO₂/TiO₂ interface, with no potential drop in the TiO₂ network. The space charge capacitance in the SnO₂ film is modulated via the modulation of the barrier height of the SnO₂/TiO₂ junction. This is justified by considering the Fermi level of SnO₂ to be lined up with the quasi Fermi level of TiO₂ at the interface. Depending on the type of applied perturbation, the modulation of the electron population at the SnO₂/TiO₂ junction has been tentatively evaluated by either assuming a classical diffusion control (potential modulation case [2]) or by using the formalism developed for IMPS (light flux modulation case [3]). The simulated profiles are in reasonable agreement with experiments. The effects of varying the experimental conditions are presently under study and will be presented at the workshop.

[1] R. Antaño-López, M. Keddad and H. Takenouti, *Electrochim. Acta* **46** (2001) 3611.

[2] R. Antaño-López, PhD Thesis, Université P. & M. Curie, Paris, novembre 2001.

[3] A.C. Fisher, L.M. Peter, E.A. Ponomarev, A.B. Walker and K.G.U. Wijayantha, *J. Phys. Chem. B* **104** (2000) 949.