

Measurement of mass/potential transfer functions
by using a fast quartz crystal microbalance

C. Gabrielli , H. Perrot and A. Rubin

UPR15 du CNRS, Laboratoire de Physique des Liquides et Electrochimie, Université P.et M. Curie, Tour 22, 4 , place Jussieu, 75252 Paris Cedex 05, France.

Since several decades, the electrochemical impedance technique has shown interesting potentialities as it allows to separate the various contributions involved in an electrochemical process. The applications are numerous and are related to various fields such as corrosion, energy storage, electroplating process, sensors, biochemistry...Then, this approach was completed by similar techniques such as EHD. Another original technique was developped very recently by using fast quartz crystal microbalance to determine a mass/potential transfer function.^{1,2}

The principle of this technique, also called electrogravimetry, is similar to the electrochemical impedance: a perturbation signal is applied to one of the electrode deposited onto the quartz resonator surface (acting as a working electrode) and the mass changes, related to this input signal, are detected through the microbalance response. In order to do this, a frequency/voltage converter is necessary to convert the microbalance frequency response in term of voltage changes. In a concrete way, the mass/potential transfer function, $\frac{\Delta m}{\Delta E}$, is determined at different polarization

values of the electrochemical system. The mass/potential transfer function and the electrochemical impedance were simultaneously measured using a four channel frequency analyzer (Solartron 1254).

In a first step, the performances of different frequency/voltage converter devices were compared by using different electronic devices and by working at different quartz resonator frequencies (6 and 9 MHz). The performances are evaluated through a calibration set up using two synthetizers. Figure 1 shows one example of the response obtained: the transfer function $\frac{\Delta V_f}{\Delta f_s}$ which

characterize the electronic device was measured over the frequency of perturbation. Thus, the sensitivity of the frequency/voltage converter, the dynamic range and also the noise were measured for different electronic configurations and at different QCM frequencies (6 and 9 MHz).

Then, the best configuration was used to examine the electrochemical behaviour of different electrochemical system. This technique appears well adapted for studying conducting polymer films. In this case, the main interest is its ability to separate the ionic contributions during the electrochemical processes. Indeed, the ionic species can be identified and the kinetic parameters easily determined. A model adapted to conducting polymer films was developped where the theoretical mass/potential transfer function were simulated. The loops obtained are related to the insertion of each ionic species involved in the charge compensation process. Moreover, it was shown that the diameter of each loop is related to the atomic mass of the ionic species (Figure 2). The free solvent motion can also be separated from the solvent accompanying the ion motions.

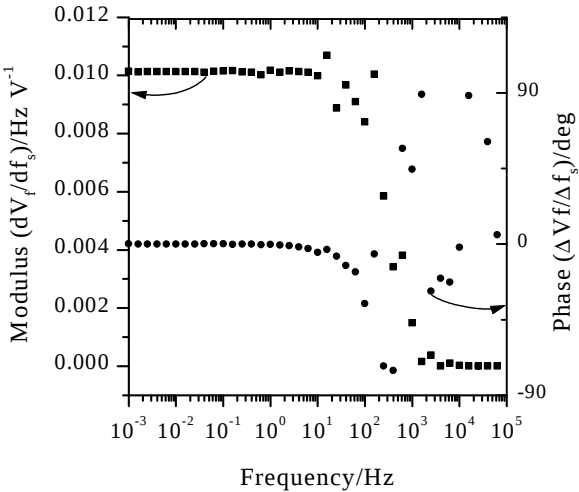


Figure 1: modulus and phases of a frequency/voltage converter used for the electrogravimetry. QCM working frequencies: 6 MHz.

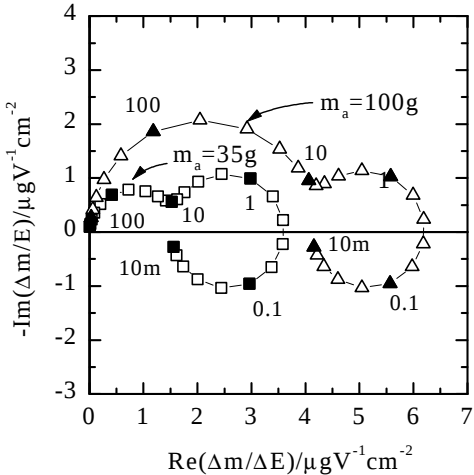


Figure 2: theoretical mass/potential transfer function with three invoved species, anion, solvent and cation. Effect of the anion size over the theoretical response: $m_a = 35 \text{ g mol}^{-1}$ or 100 g mol^{-1} .

References

[1] C. Gabrielli, J. J. García-Jareño, M. Keddad, H. Perrot et F. Vicente, J. Phys. Chem. B, 106(2002)3182-3191.
[2] C. Gabrielli, J. J. García-Jareño, M. Keddad, H. Perrot et F. Vicente, J. Phys. Chem. B, 106(2002)3192-3201.