

New multi-scale approach based on *ac*-electrogravimetry, for characterizing insertion materials.

C. Gabrielli^{1,2}, T.H. Ho^{1,2}, C. Laberty-Robert³, H. Perrot^{1,2}, O. Sel^{1,2} and M. Turmine^{1,2}.

1. CNRS, UPR 15 du CNRS, LISE, 4, place Jussieu, 75252 Paris, France.

2. Université P. et M. Curie, LISE, 4, place Jussieu, 75252 Paris, France.

3. LCMCP-CNRS-UMR-7574-Collège de France, 11, place Marcelin Berthelot, 75231 PARIS France.

Many in-situ methods of investigation were developed for characterizing battery materials. Electrochemical Impedance Spectroscopy (EIS) methodology offer very attractive potentialities in term of understanding what happens in many insertion films like battery materials. Advantages are related to the fact that the frequency modulation allows an easy and fast separation of the electrochemical process to be obtained. Nevertheless, in many cases, the EIS diagram interpretation is not so easy which is correlated very often to the difficulties obtaining a pertinent model. Transport and transfer characterizations of the different ionic species are not easily achieved. To solve this problem, a coupling between EIS technique and quartz crystal microbalance (QCM) measurements is possible. In this case, the appropriate material is deposited on one of the gold electrode of a quartz resonator. Two kinds of complementary characterization can be obtained at the same time, electrochemical and gravimetric, which leads to a new multi-scale experimental technique also called *ac*-electrogravimetry. By using a specific and fast QCM, a new transfer function can be determined, $\Delta m/\Delta V(\omega)$ in complement with the classical, $\Delta V/\Delta I(\omega)$.

The principle of *ac*-electrogravimetry, is similar to 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, $\Delta m/\Delta V(\omega)$, 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 this case, the main interest is its ability to separate the ionic contributions and free solvent during electrochemical/chemical processes.¹ Indeed, the ionic species and the solvent can be identified and the kinetic parameters easily determined. Different models adapted to these films were developed where the theoretical mass/potential transfer functions were simulated. The loops obtained are mainly related to the insertion of each species involved in the charge compensation process.

In a first step, different films were tested in order to validate this new methodology of in-situ measurement. Electronic Conducting Polymers (PCE) offer the advantage of an easy making and a high stability. For that reason, *ac*-electrogravimetry was performed with

polyaniline and polypyrrole materials. These films were easily electrogenerated. One example of *ac*-electrogravimetry measurement is given in figure 1 for polypyrrole made in paratoluene sulfonate (pTs). In the $\Delta m/\Delta E(\omega)$ transfer function allows the anion and free solvent can be identified. The kinetics constant rates and the relative concentration changes were estimated over the different potential values.

Different models were developed in order to describe the electrochemical behaviour of these films. A basic model can be used and was based on the ionic transfer between the film and the electrolyte. Unfortunately, good fitting are not easily reached in this case. Therefore, more sophisticated models are necessary by taking into account electronic transfer, porosity of the material and parasitic electrochemical reactions.

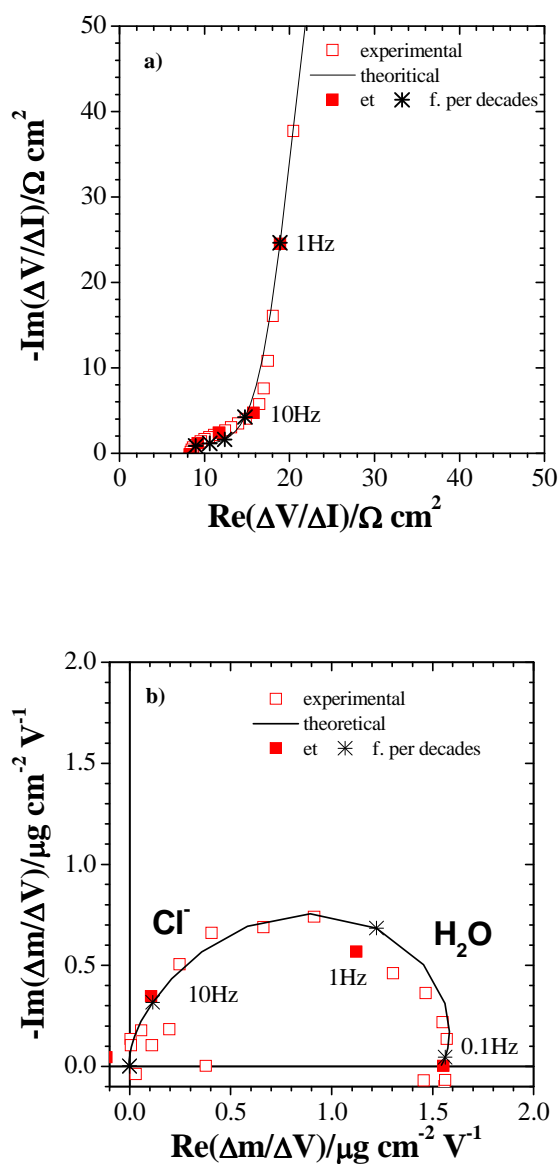


Figure 1 : Transfer functions obtained for PPy-pTs in NaCl 0.25 mol L⁻¹ at -0,2 V vs AgAgCl; a) $\Delta E/\Delta I(\omega)$ and b) $\Delta m/\Delta E(\omega)$.

Reference:

1. C. Gabrielli and H. Perrot, "ac-electrogravimetry investigation in electroactive thin films", ed. by M. Schlesinger, Springer, 2009, p151-231.