Investigation of Transport/Insertion Processes in Mixed and Ionic Conducting Thin Films by Ac electrogravimetry.

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It is now commonly admitted that ions and solvent may be both involved during the switching between oxidation states of electroactive materials. Despite the numerous past studies, there are still many remaining questions regarding the kinetics of the transport and insertion of these species during this redox process. The usual techniques used to investigate the charge compensation are based on the analysis of the current and mass responses to a potential scan by means of a potentiostatic arrangement coupled with a quartz crystal microbalance.

However, the frequency analysis of both current and mass which allows a real dissection of the whole process and the separation of the movements of each species has been shown to be a powerful technique to investigate the redox processes of electroactive thin films. This is ac-electrogravimetry, where the usual impedance, $\Delta E / \Delta I(\omega)$, is simultaneously measured with the mass/potential transfer function, $\Delta m / \Delta E(\omega)$. This technique allows the change of mass related to a charge unit passing through the electrode/polymer/solution interfaces to be determined. Therefore, all the species involved in the charge compensation process occurring during the redox switching of an electroactive thin film can be separately identified by their atomic mass.

The experimental set up used, based on a 4 channels frequency response analyser (FRA), allows the impedance and the mass-potential transfer function to be simultaneously measured. The latter is obtained by using a fast quartz crystal microbalance [1, 2].

This new technique can be applied to mixed conducting materials like conducting polymers (e.g. polyaniline, polypyrolle) [1] and even to ionic conductors (Nafion, protonic membranes) [3]. For the latter, a mixed mediator film has to be used. Figures 1 and 2 show example of the investigation of Nafion coating Prussian Blue as the mediator film which allows protons to be exchanged between the protonic film and the mediator film which exchanges electrons with the gold electrode of the quartz crystal. For a mixed conducting material like polyaniline, anions, cations, and solvent both transfer from the solution to the film and electrons transfer from the film to the electrode.

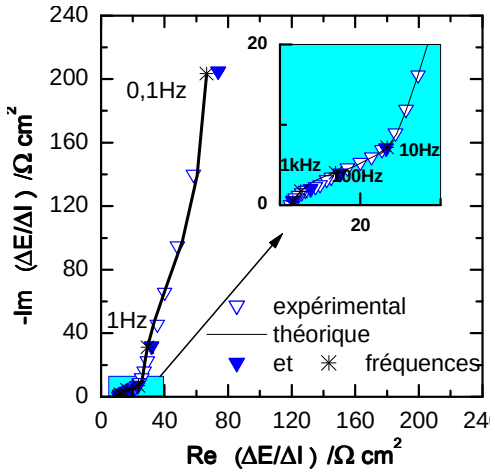

Figure 1: Experimental electrochemical impedance obtained on Prussian Blue/Nafion composite film in KCl 0.15 M at E = 0.25 V vs SCE.

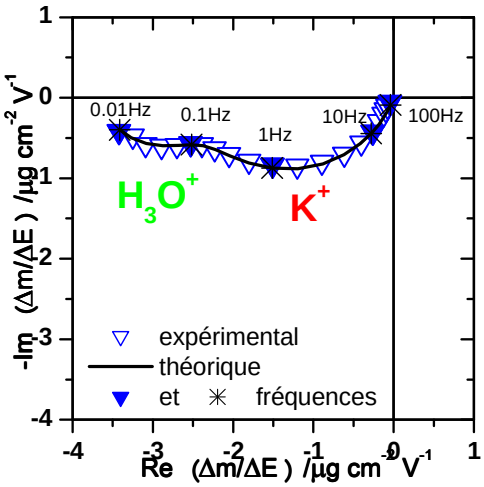

Figure 2 : Experimental mass-potential transfer function obtained on Prussian Blue/Nafion composite film in KCl 0.15 M at E = 0.25 V vs SCE.

References

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3- L. To Thi Kim, O. Sel, C. Debiemme-Chouvy, C. Gabrielli, C. Laberty-Robert, H. Perrot et C. Sanchez, Electrochem. Com., 12 (2010) 1136.