

AC-ELECTROGRAVIMETRY STUDY OF POLYPYRROLE

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Conducting polymers are very attractive materials considering their large application fields. Nevertheless, some shade remains towards the electrochemical mechanism of these films. A huge step would be to fully understand their electrochemical behaviour. For this goal, the coupling of electrochemical impedance and electrogravimetric transfer function techniques may broaden this horizon.

Measurements were carried out by means of a conventional potentiostatic set-up coupled with a home made fast quartz crystal microbalance. The impedance and the mass/potential transfer function were simultaneously measured using a four channel frequency analyser (Solartron 1254).

This work was focused on polypyrrole films. These films were prepared from 0.1M pyrrole solutions and were polymerized under controlled current onto 9 MHz quartz resonator gold electrode. Electrochemical experiments were carried out by using a classical three electrode cell filled with 0.5M KCl solution. Then, the modified working electrode is polarized at a chosen potential. The mass change due to ionic insertion in the film is detected through the quartz microbalance frequency changes. These changes are sent to a homemade frequency/voltage converter connected to the analyser.

First of all, we can notice that for thin polymer film, the rate-limiting step is due to the ionic transfer between the solution and the film since the electrochemical impedance $\frac{\Delta E}{\Delta I}(\omega)$ has no slope equal to 45° in the low frequency range (Fig. 1). Then, electrogravimetric transfer function $\frac{\Delta m}{\Delta E}(\omega)$ shows cation or anion motions distinguishable (Fig 2.). By this way, we are able to identify the ionic species involved in the switching process as each loop is linked to one specie: the loop located in the first quadrant is related to an anion entry. Moreover, the diameter of the loop characterises the molecular weight of the involved species and the frequencies, the kinetic of insertion (Fig 3).

The ionic compensation phenomena is a characteristic of the redox switching of the electroactive polymer. *ac*-electrogravimetry allows the anion, cations and solvent transfer at the polymer/electrolyte interface to be separated. Moreover, we are able to determine the time constant of their relaxation.

References

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2. C. Gabrielli, J. Garcia-Jareño, H. Perrot, *Electrochimica Acta* 46 (2001) 4095-4103.

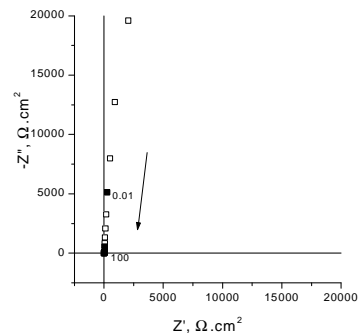


Fig. 1: Electrochemical impedance of a polypyrrole film in 0.5M KCl electrolyte at 0.1V/SCE

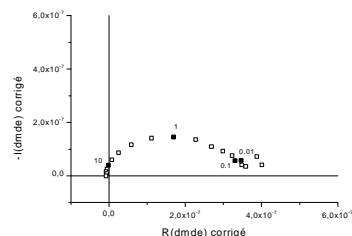


Fig. 2 - Electrogravimetry transfer function of a polypyrrole film in 0.1M KCl electrolyte at +0.3V/SCE.

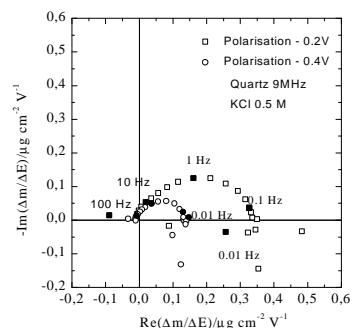


Fig. 3 – Electrogravimetry transfer function of a polypyrrole film in 0.5M KCl electrolyte.