Ionic transfers in a polypyrrole film by electrogravimetry

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After the first reported work by DeBerry [1] on the corrosion protection of metals by Conducting Polymers (CP), there have been many attempts both to propose a comprehensive mechanism as well as to improve their efficiency. In a previous study, a good protection efficiency for Polypyrrole (PPy) films grown on iron using electropolymerization in a potassium tetraoxalate solution was demonstrated in 3% NaCl corrosive test solutions [2]. Open circuit potential and EIS measurements basically supported an anodic protection mechanism. In a first stage, chloride ions were found to be exchanged with oxalate anions till their contact with the inner passive film and its further breakdown. Healing of the associated pits was achieved through ferrous oxalate precipitation as long as oxalate anions are available and finally iron corrosion starts after delamination of the film.

Progressive dedoping of PPy was observed with a decreasing ionic mobility. However, for rather reduced conditions, a new increased ionic mobility was observed and that effect was ascribed to ingress of cations thus indicating a change in the permselectivity.

The Electrogravimetry technique is a variant of the EQMB, which is based on the analysis with frequency of the mass modulation in response to a potential modulation of low amplitude, therefore fulfilling the requirements of an impedance technique. This technique was shown to allow for unravelling of separate contributions of anions, cations and solvent [3].

Simultaneous measurement of mass (Δm), current (ΔI) and potential (ΔE) variations with frequency ω/2π (Hz) allowed for the calculation of the Electrochemical Impedance ΔE/ΔI(ω) and transfer functions such as Δm/ΔE(ω) or Δm/Δq(ω).
For example, one can show that [3] :

$$\frac{\Delta m}{\Delta E}(\omega) = d\left(m_c \frac{-G_c}{j\omega d + K_c} + m_a \frac{-G_a}{j\omega d + K_a} + m_s \frac{-G_s}{j\omega d + K_s} \right)$$

where d is the film thickness, m_c, m_a and m_s are the molecular weights of the cation, the anion and the solvent respectively. G and K parameters stand for combinations of the reaction rates of the doping reactions and concentrations in and out of the exchanged ions.
The sign of G can be positive (ion expulsion) or negative (ion insertion).

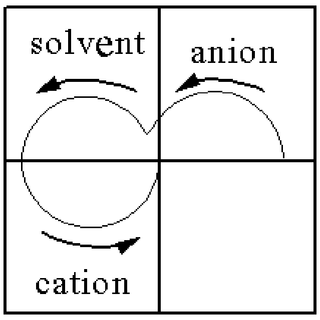

Figure 1 :
Simulation of the transfer function Δm/ΔE in the case of cation expulsion and anion and solvent insertion. Each loop with its characteristic time constant is related to a particular specie.

Figure 1 depicts the aspect of the Δm/ΔE (ω) transfer functions in the case of mixed ionic exchange. In some simple cases, this transfer function only shows one loop and therefore the exchange of a single specie as expected from the ideal case.

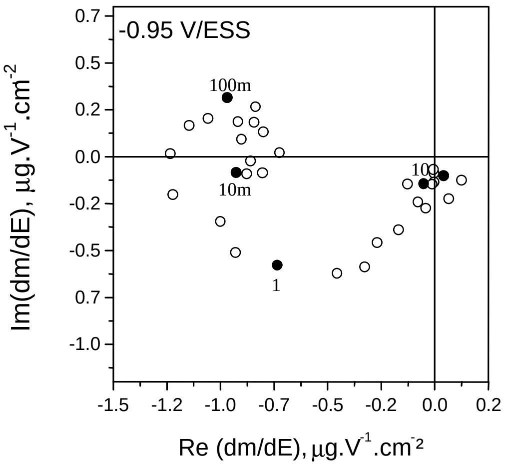

Figure 2 : Experimental Δm/ΔE transfer function at E= -0.95V/SSE

The used quartz has an AT cut and oscillates at 9 MHz. On the golden face in contact with solution is grown a PPy film in galvanostatic mode (*ca* 100 nm thick). The synthesis solution contains potassium tetraoxalate (0.05 M.L^{-1}) and Pyrrole (0.1 M.L^{-1}).

As an example, the diagram in Figure 2 in the cathodic range –but at which the PPy is not completely reduced- shows actually three loops which corroborates the contribution of the cation already invoked in [2].

Analysis of the mass impedance diagrams was consistent with the contribution of the chloride, of sodium and water.

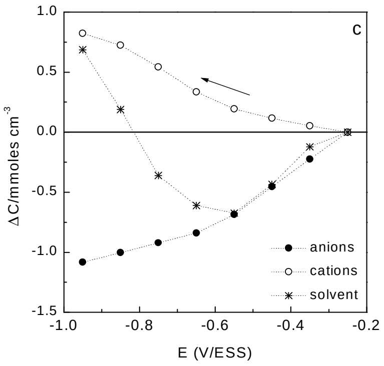

Figure 3 :
Potential dependence of the concentrations of the three species in the film

The results of the analysis could be summarized in the curves of Figure 3 showing that from anodic to cathodic potentials and till a potential of *ca* – 0.6 V/SSE, the main contribution to dedoping would be the expulsion of anions accompanied by solvent.

At lower potentials the insertion of cations would be predominant with solvent going in the same direction.

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