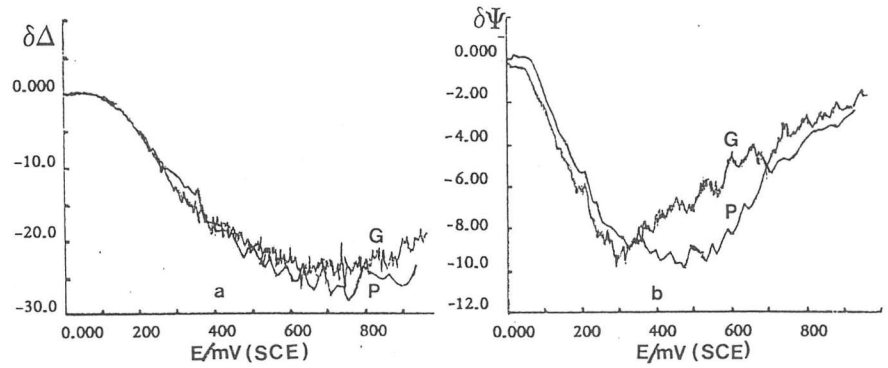

Fig.4 : Comparison of the ellipsometric data, delta (a) and psi (b) measured at 725 nm, during galvanostatic (G) and potentiostatic (P) PMeT growth.

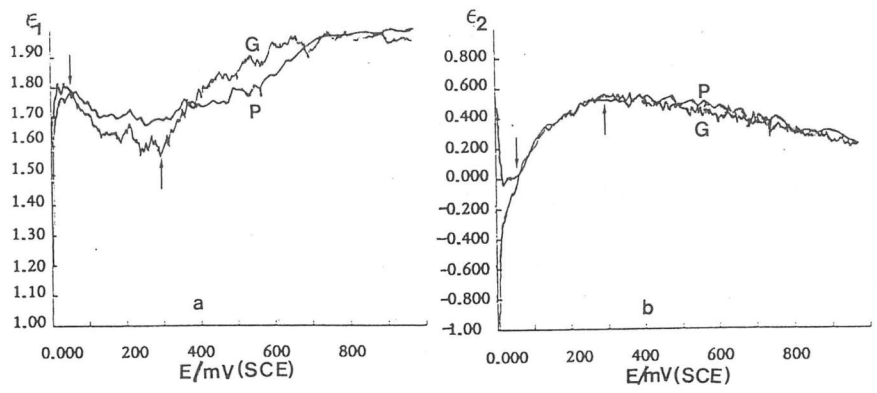

Fig.4 : Real (a) and imaginary (b) part of complex dielectric constant for PMeT (↓) denotes the start of first layer and (↑) the transition for a second layer formation.

THE ROLE OF THE "CHARGING CURRENT" IN THE ELECTROCHEMICAL BEHAVIOUR OF POLYPYRROLE

L.M. Abrantes[1], J.C. Mesquita[1], M. Kalaji[2], L.M. Peter[2]

[1]CECUL (INIC), Department of Chemistry, Faculty of Sciences, 1294 Lisboa Codex, PORTUGAL

[2]Department of Chemistry, The University, Southampton SO9 5NH, UK

In spite of the extensive research in the area of conducting polymers during the past few years, as a result of the interest in potential applications of these materials, the interpretation of some aspects of their electrochemical behaviour is still controversial **[1]**.

In the electrochemical behaviour of different conducting polymers the appearance of current plateaus after the voltammetric peaks is characteristic and was attributed to a double layer charging **[2]**. The a.c. impedance is used as a technique to evaluate the nature of that current plateau **[3]**, but the expected Warburg behaviour is not observed. As pointed out by Rubistein *et al* **[4]**, it is not possible to distinguish a non-faradaic double layer capacitance from a faradaic pseudo-capacitance on the basis of electrical measurements alone.

The relationship between electrical and optical a.c. response has been recently discussed **[5,6]** and the simultaneous analysis of the periodic electrical and optical response of PANI modified electrodes was shown to be related with Faradaic processes **[6]**.

In the present study modulated transmittance was applied to characterize polypyrrole (PPy). Thin PPy films were electrosynthesized on optical transparent electrodes, ITO, from pyrrole in acetonitrile. A typical cyclic voltammogram is shown in figure 1-a) together with the optical absorbance change at 550 nm. The absorbance increase, even after the peak current, varies linearly

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with the charge, figure 1-b). The hysteresis suggests non reversible structural changes.

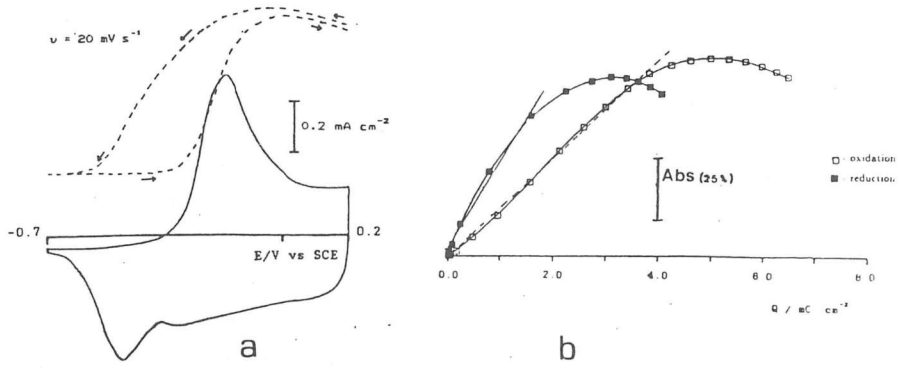

Fig. 1 - a) Cyclic voltammogram of 100 nm PPy film and simultaneous optical absorption change, λ = 550 nm (- - -).

b) Absorption vs charge.

Figure 2 compares the Bode plot of the impedance of the equivalent circuit for a polymer film-coated ITO electrode **[6]** with the Bode plot of the impedance of thin PPy films and shows the validity of assuming the same approach.

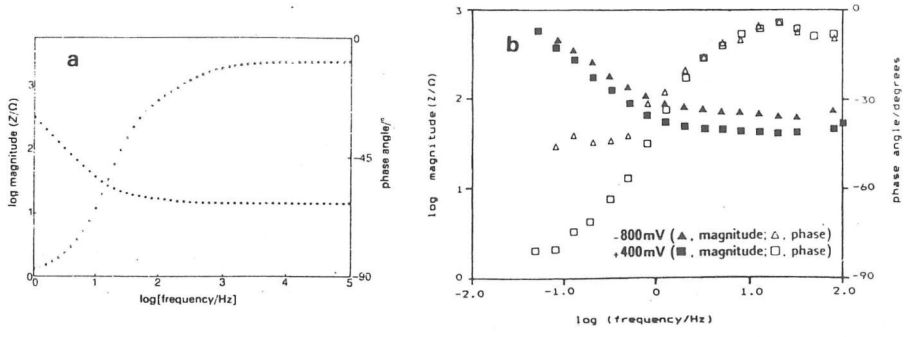

Fig. 2 - a) Bode plot of the impedance of the equivalent circuit described in reference 6.

b) Bode plot of the impedance of a 100 nm PPy film.

Conformational changes in PPy films are likely to occur at long time scales. As illustrated in figure 3 the capacitance measured using small amplitude perturbation at constant d.c. potential is lower than the pseudo-capacitance derived from the voltammogram. Therefore the quantity of charge transferred in PPy under small amplitude periodic perturbation is lower than during a potential scan.

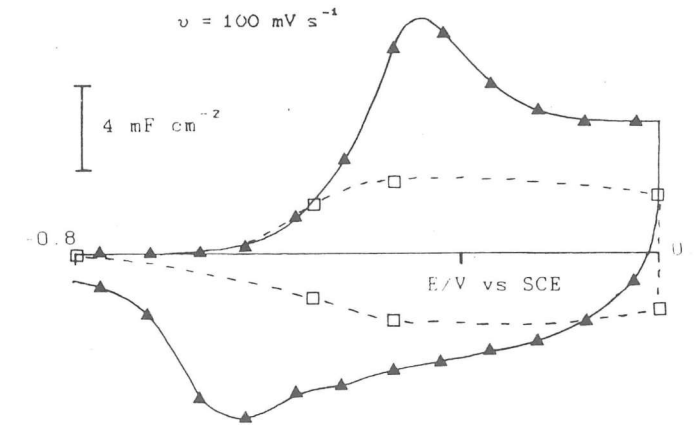

Fig. 3 - Capacitance of a 100 nm PPy film determined from impedance (□) and derived from cyclic voltammogram (▲).

The correlations between electrical and optical response are analysed in terms of complex plane plots (figure 4). Taking into account that the electrical terms (capacitance, impedance and admittance) become identical with their optical analogues only in the case where non-faradaic processes make no contribuition to the total current, the similar characteristic relaxation fraquency observed in figures 4-a) and 4-b) reveal that the a.c. response for PPy is dominated by Faradaic processes.

The agreement about the meaning of the "charging current" for PANI and PPy films is very probably extensible to other polymer systems.

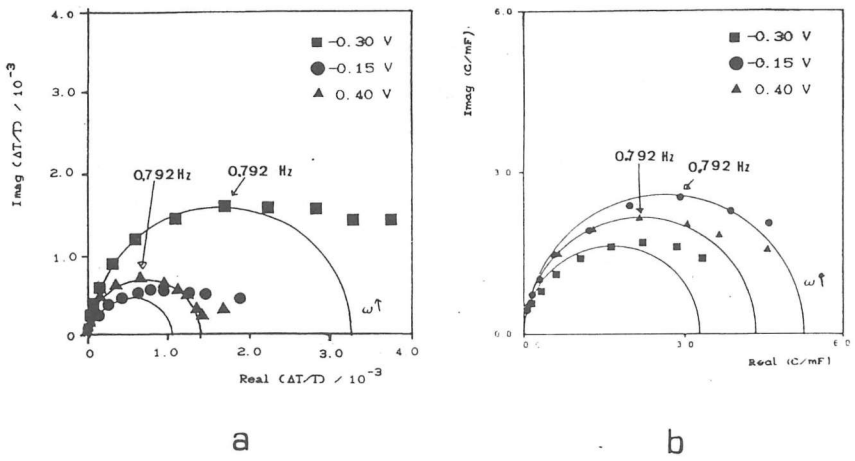

Fig. 4 - Complex plane plots
a) modulated normalized transmittance
b) complex capacitance

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DIGITAL SIMULATION APPLIED TO THE IDENTIFICATION OF THE OXIDATION MECHANISM OF $[FeH(CNMe)(dppe)_2][BF_4]$

M. Amélia N.D.A. Lemos, Armando J.L.O. Pombeiro
Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Lisboa

ABSTRACT

The anodic behaviour of an hydride-isocyanide iron(II) complex, $[FeH(CNMe)(dppe)_2][BF_4]$, was investigated using a digital simulation computer program applied to cyclic voltammetry experiments. The proposed mechanism is of an ECECE type, and the homogeneous rate constants were evaluated.

RESULTS and DISCUSSION

The anodic oxidation of the iron(II) complex $[FeH(CNMe)(dppe)_2][BF_4]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) was studied by cyclic voltammetry, at a platinum electrode, in a 0.2M $[Bu_4N][BF_4]$/THF electrolyte solution, and by controlled potential electrolysis at a platinum gauze in the same electrolyte solution, as described previously [1].

The cyclic voltammogram shows two anodic waves. The current function for the first wave increases for lower scan rates, whereas the second wave disappears at high scan rates.

The number of electrons involved, as determined by c.p.e., are two for the first wave and one for the second wave.

The product obtained by controlled potential electrolysis at the first wave was isolated from the electrolyte solution and identified as the fluoro-isocyanide complex of iron(II) $[FeF(CNMe)(dppe)_2][BF_4]$; its cyclic voltammogram shows a single-electron reversible oxidation wave at $E_{1/2}$ coincident with that of the above mentioned second wave.

Through the analysis of these results and comparison with published data [2], we have proposed the ECECE mechanism for the anodic behaviour of that complex indicated in the

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