

Investigations of the redox mechanism of poly(5-amino-2-methyl-1,4-naphthoquinone) (PAMNQ) by in situ FTIR, EQCM and Electrochemical Impedance.

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Recently, a novel conducting polymer, poly(5-amino-1,4-naphthoquinone) (PANQ) has been developed in our group [1]. In organic electrolyte, the quinone / hydroquinone redox couple is reversible and very stable in the domain -1.25 / -0.20 V vs Ag/AgCl. The polymer exchanges cations for the charge-compensation process. In LiClO₄/acetonitrile electrolyte, lithium ions can be inserted and expelled reversibly. PANQ was then studied as an electrode material for lithium-ion batteries [2]. The p-doping of the polymer chain occurs in the positive potential domain but it is not reversible and not quite stable in organic medium [3].

In order to improve the electrochemical performance of the system, a new substituted monomer was considered : 2-methyl-5-amino-1,4-naphthoquinone (MANQ), which is the subject of this communication. The monomer synthesis was developed and achieved in the laboratory and poly(2-methyl-5-amino-1,4-naphthoquinone) (PMANQ) film was electrochemically grown. PMANQ film presents two distinct redox systems, the quinone group and the π -conjugated system. A similar system poly(1,5-diaminoanthraquinone) has been described recently [4].

Simultaneous voltammetric and d.c. conductimetry measurements have shown that this film is conducting in a large potential domain, between -1.2 V and +1.2 V vs SCE, probably via its two polaronic forms : the positive (NH⁺) and the negative (Q⁻) ones (Fig. 1).

The redox mechanisms of the film were studied by Multiple Internal Reflection Fourier Transform Infrared Spectroscopy (MIRFTIRS, Fig. 2), supported by in-situ Electrochemical Quartz Crystal Microbalance (EQCM) and impedance (EIS). Interactions between quinone and amine groups (hydrogen bonds, redox reactions) were evidenced. Interactions have been already described in the literature between polyaniline and dissolved quinones [5]. Here, these functional groups are on the same polymer moiety.

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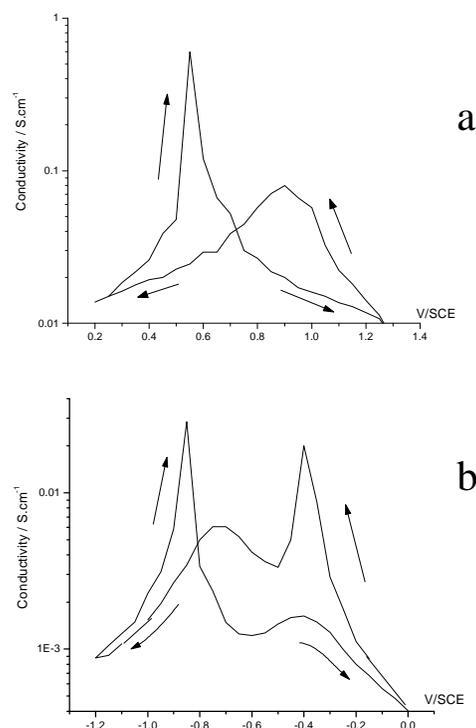


Fig. 1 : In-situ conductivity curves of PAMNQ in a 0.1 M LiClO₄/ ACN solution at 5 mV.s⁻¹ in the potential ranges 0.2 to 1.25 V(a), and 0 to -1.2 V vs SCE (b).

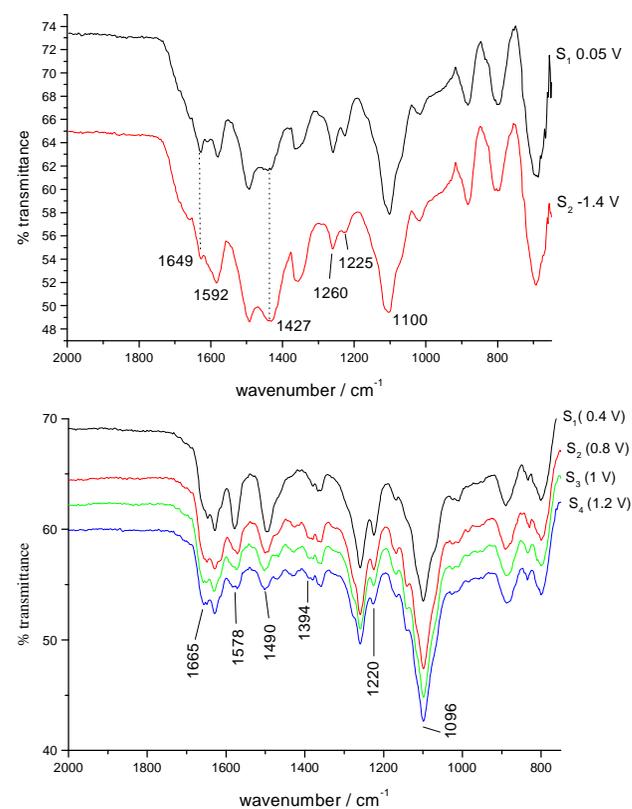


Fig. 2 : In-situ MIRFTIRS spectra recorded during PAMNQ electroactivity in 0.1 M LiClO₄/ acetonitrile in the negative and the positive potential ranges