One-step Electrosynthesis and Characterization of Poly(aniline)–Nafion and Poly(3-methylthiophene)–Nafion Composite Films

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Impregnated polymer composites, poly(aniline)–Nafion and poly(3-methylthiophene)–Nafion have been electrosynthesized from a solution containing a perfluorosulphonated ionomer (Nafion) as the only electrolyte and the monomer precursor of the electronically conducting polymers: poly(aniline) or poly(3-methylthiophene).

Composite materials made from an electronically conducting polymer (ECP) matrix impregnated with another component of ionomer type (Io) which acts to provide dopant anions, have attracted considerable interest.[1—9c] In particular, the coupling of cationic membrane properties with conductive polymer properties results in a 'charge controllable membrane' with cation-exchange properties.[9a—c] These cation-exchange properties with mixed conductivity (ionic and electronic) behaviour and faster kinetics of redox exchange,[1,10] have applications in water deionization,[9b] batteries,[9c] sensors (by preconcentration of cations), SPE† assembly for fuel cells, and 'smart windows.' From the literature survey, recent work on the electrochemical synthesis of these composites, ECP/Io, may be categorised according to the approach taken. (a) Inclusion of the electronically conducting polymer in an ionomer membrane film predeposited at the surface of the electrode. We call this the two-step method: dip-coating, then electropolymerization. (b) Electrosynthesis of the composite directly from a solution containing both the dispersed ionomer and the monomer precursor of the polyaromatic polymer. We call this the one-step method.

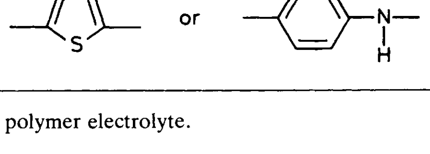
Amongst the selection of polyelectrolytes, Nafion has received increasing attention because of its high ionic conductivity and unique chemical characteristics.[11]

The two-step syntheses of such Nafion composites have involved mainly poly(pyrrole), PPy, but recently have been extended to poly(thiophene), PT,[3b] poly(3-methylthiophene), PMT,[10,12] and poly(aniline), PANI.[10] Ionomers are often only solubilized in aqueous solvents inadequate for PT or PMT electrosynthesis,[13] whilst PANI needs an aqueous acid medium for growth. For instance, one-step electrosynthesis of the composite poly(aniline)–poly(styrenesulphonate) can be performed successfully from an aqueous solution of poly(styrenesulphonic acid) acidified with $HClO_4$ (0.1 M).[14]

The novel routes reported here are the one-step electrosynthesis of PMT–Nafion and PANI–Nafion composites from: (a) a solution of Li^+ Nafion (Li^+ exchanged) in anhydrous propylene carbonate, PC, (b) a solution of H^+ Nafion in 2% aqueous acetonitrile (without addition of any other acid), respectively. Compared with the two-step method, the one-step electrosynthesis is more suitable for ensuring a well defined stoicheiometry between the positive charges of the ECP matrix (doping level) and the sulphonic pendant groups of the Nafion structure.[2] This is the result of a homogeneous structure, in contrast to phase segregation which sometimes occurs in two-step synthesized materials.[3a]

$$n\mathrm{RH_2} + \delta n\ \mathrm{SO_3^-}\!\sim\!\sim \xrightarrow{-n(2+\delta)e^-} (\text{-R-}^{\delta+},\ \delta\ \mathrm{SO_3^-}\!\sim\!\sim)_n + 2n\mathrm{H^+} \qquad (1)$$

where R ≡



The preparation of organic solutions of Nafion, either anhydrous or with a low water content, has been made possible by the use of a suitable Nafion powder.‡ The overall electrochemical reaction is given in equation (1), where δ is the doping level. The wavy line adjoining SO_3^- symbolizes the perfluorinated Nafion matrix.

Films of PANI–Nafion were grown on a platinum electrode (geometric area, $S = 3$ mm^2) by controlled potential oxidation at 0.75 V§ of a 0.01 M aniline solution in aqueous acetonitrile (1.6% H_2O) containing Nafion (0.02 M). As charges are consumed, two main redox couples appear in the anodic region ($E°_1 = -0.08$ V, $E°_2 = 0.5$ V). Contrary to the voltammetric curves reported by previous workers relating to the preparation of poly(aniline) in an organic medium,[15] these peaks are very well shaped. Increasing the charge results in a regular growth of the anodic and cathodic observed peak currents (Figure 1), confirming the increasing thickness of an electroactive PANI–Nafion film. The third middle redox system¶ often observed in poly(aniline) voltammetric curves and recently explained in terms of cross-linking[16] is quasi-absent here (small shoulder at 0.42 V), accounting for a more regular structure than the classical aqueous H_2SO_4 prepared PANI.

After a 0.20 C cm^{-2} deposition, the polymer-modified electrode was thoroughly rinsed and transferred to a clean solution of $LiClO_4$ (0.1 M) in anhydrous acetonitrile. Scanning the electrode in the anhydrous medium again shows two main reversible systems, 1/1′ and 2/2′ located at 0.12 and 0.97 V respectively, with a weak middle system 3/3′ at 0.52 V and a pre-peak 4 at −0.2 V (Figure 2A). Surprisingly, if compared with previous reported voltammograms obtained for organic and aprotic media,[17] the electrochemical response of this PANI–Nafion composite remains well defined in this aprotic medium. It can be assumed that the Nafion matrix plays the role of a proton sponge, and of a protonic conductor, and may help the proton transfer needed for the PANI electroactivity.[18] Moreover, the water content greatly influences the electroactivity of PANI.[18] This role is dramatically sensitized

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† SPE = solid polymer electrolyte.

‡ This powder has been prepared by precipitation from a commercial Aldrich aqueous alcoholic solution of Nafion 117 (in the protonic form), which was submitted to a vacuum at room temperature overnight. The Li^+ Nafion powder was synthesized by exchange of the H^+ Nafion powder using a dry acetonitrile solution of $LiClO_4$, in which the Nafion powder is almost insoluble.

§ All potentials were measured *vs.* an Ag/10^{-2} M Ag^+ reference electrode prepared in MeCN, the potential of which is 0.344 V *vs.* a normal hydrogen electrode (NHE) (in water). In PC we use the same reference electrode, neglecting the junction potential.

¶ When PANI is prepared in the classical aqueous H_2SO_4 (1 M) solution, a third redox ill-defined system appears between the two main redox systems 1/1′ and 2/2′. This electroactivity has been assigned to phenazinic units, appearing by reticulation of PANI chains.[16]

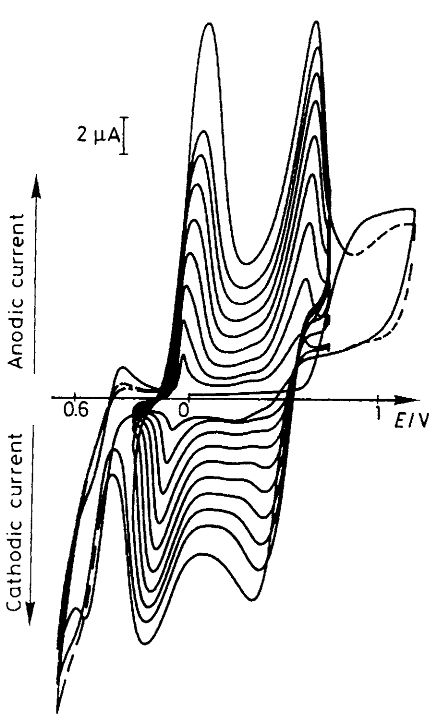

Figure 1. Successive cyclic voltammograms, v = 10 mV s^{-1}, on a Pt electrode (S = 0.03 cm^2) in MeCN, 1.6% H_2O, containing aniline (10^{-2} M) and H^+ Nafion (2×10^{-2} M). 2×10^{-4} C are passed at a controlled potential of 0.75 V (*vs.* Ag/10^{-2} M Ag^+) between each voltammogram.

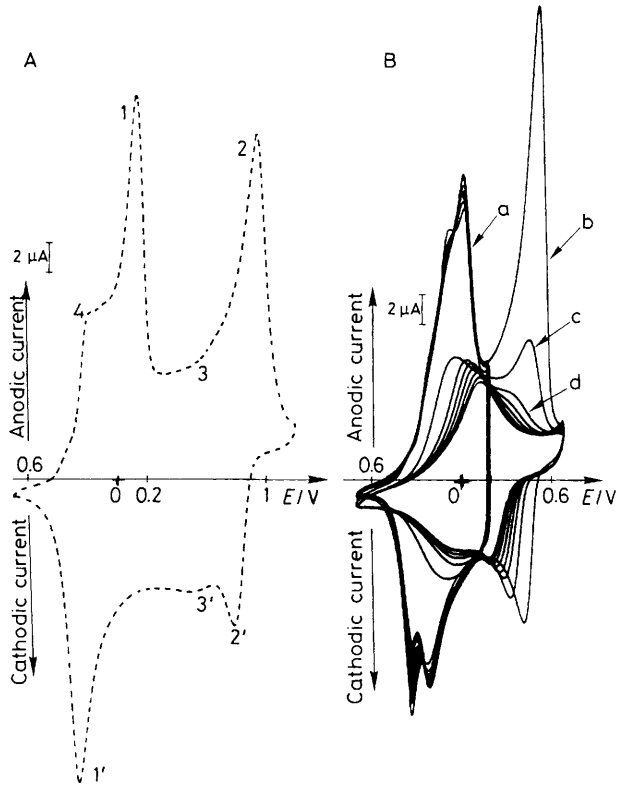

Figure 2. Cyclic voltammetry, v = 10 mV s^{-1}, of a Pt/PANI–Nafion electrode (S = 0.03 cm^2) after 6×10^{-3} C deposition of the composite under the conditions of Figure 1; A, (- - -) in MeCN, $LiClO_4$ (0.1 M); B, (——) after addition of 5% H_2O; (a) successive scans from −0.7 to + 0.18 V; (b), (c) *etc.*, successive scans after extending the potential range to 0.69 V.

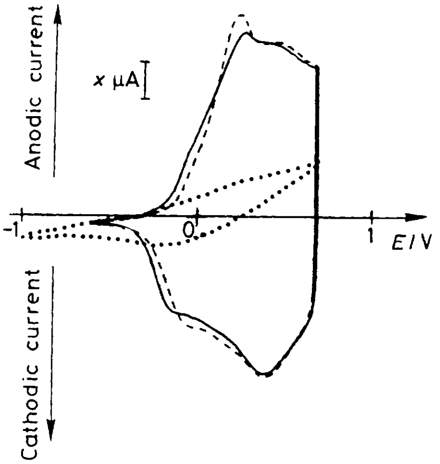

Figure 3. Cyclic voltammetry curves on a Pt (S = 0.03 cm^2) electrode; (· · ·) in dry PC containing Li^+ Nafion (10^{-2} M) and 3-methylthiophene (10^{-1} M) after passing 10^{-2} C at a constant current of 200 μA, v = 20 mV s^{-1}, x = 10; (——) after transferring into a $LiClO_4$ propylene carbonate solution (0.1 M), v = 5 mV s^{-1}, x = 2; (- - -) after transferring into a 0.1 M solution of $LiClO_4$ in MeCN, v = 5 mV s^{-1}, x = 2.

by the Nafion matrix, as suggested by the significant cathodic shift (0.23 V) of the second redox system after addition of 5% H_2O (Figure 2B). The Nafion membrane does not work in the dry acetonitrile medium.[19]

In the anhydrous medium, the electrode is fairly stable towards electrochemical cycling (4% electroactivity loss after 500 cycles), whilst in the hydro-organic acetonitrile medium, the composite polymer is stable only if the scanning is restricted to the first anodic redox system (Figure 2B); it quickly degenerates when the second system is reached (Figure 2B, b). The same phenomenon is observed when cycling in an aqueous (1.6% H_2O) 0.02 M H^+ Nafion in acetonitrile medium and is increased with increasing concentration of water (5% H_2O).

Figure 3 shows the cyclic voltammetry curve obtained on a platinum electrode (S = 3 mm^2) in dry PC containing Li^+ Nafion (0.01 M) and 3-methylthiophene (0.1 M), after passing 0.01 C at a constant current of 7 mA cm^{-2}. The very broad response could be explained, in part by the high ionic resistivity of this dry Nafion solution; however, addition of water (10%) (to this electrosynthesis medium) after the film deposition does not change significantly the electrochemical response. This behaviour is quite different from that of the composite PPy–Nafion in MeCN–H_2O,[2] but is the same as that of PPy–Nafion in a PC medium. Experiments are in progress to explain this behaviour. After transferring the PMT–Nafion modified electrode, with thorough rinsing, to a 0.1 M solution of $LiClO_4$ in anhydrous PC or MeCN, the cyclic voltammetry curves appear very similar to those of classical poly(3-methylthiophene) with a doping level of 20%, the commonly reported value.‖ After 2500 cycles (from −0.6 to 0.7 V) in 0.1 M $LiClO_4$ in MeCN, we observed only a 13% loss in electroactivity.

In conclusion, the commercial aqueous alcoholic solution of H^+ Nafion cannot be used directly for the one-step synthesis of the composites PANI– and PMT–Nafion. We have shown that the use of Li^+ Nafion powder in solution in dry PC allows

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‖ The doping level δ is calculated according to the formula: $\delta = 2Q_r/(Q_s - Q_r)$, where Q_s is the charge used for the electrodeposition and Q_r the charge under the oxidation peak of the polymer.

the electropolymerization of 3-methylthiophene. Moreover, a H^+ Nafion solution in 1.6% aqueous MeCN is sufficiently acidic to allow the electropolymerization of aniline without the addition of a supplementary inorganic acid. These polymer films appear fairly stable, and especially in the case of PANI–Nafion exhibit new redox properties in the organic medium resulting from the coupling of the redox behaviour of the ECP with the cationic membrane behaviour of Nafion.

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