

## New Chemical Synthesis of Mixed Conductivity Polymers

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Polymer alloys with mixed electronic and ionic conductivity have been synthesized from perfluorosulphonated ionomer membranes (bulk or solution) and monomer precursors of electronically conducting polyaromatic polymers such as polypyrrole or polyaniline.

In recent research, we became involved in preparing some mixed conductivity polymers (M.C.P.) whose main characteristic is to superpose the electronic conducting properties of a polyaromatic skeleton and the ionic conducting properties of a perfluorosulphonated membrane. From the literature survey, recent work may be summarized through two major approaches: on one hand, chemical<sup>1</sup> or electrochemical<sup>2-4</sup> inclusion of the electronically conducting polymer in the ionomer membrane and, on the other hand, electrosynthesis

of the M.C.P. directly from a solution containing both the dispersed ionomer and the monomer precursor of the polyaromatic polymer.<sup>4</sup>

In this communication we propose some alternative chemical pathways for obtaining M.C.P. films. We also report an original result concerning the electrochemical behaviour of a Nafion® doped polypyrrole film.

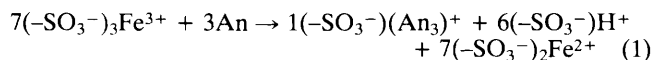
Our first synthetic procedure consists of including polypyrrole or polyaniline in commercial Nafion® 117 membranes

**Table 1.** Significant characteristics for several M.C.P. films chemically prepared from Nafion® 117 membranes with different aqueous solutions of oxidizer and monomer; Pyr = C<sub>4</sub>H<sub>3</sub>N, An = C<sub>6</sub>H<sub>5</sub>N, Nf = C<sub>19</sub>F<sub>38</sub>O<sub>2</sub>.

Oxidizer	Monomer	$\sigma$ (S cm <sup>-1</sup> ) (Monomer side)	M.C.P. <sup>a</sup> Crude formulae	M.C.P. Developed formulae	C.P. Doping level	Weight ratio C.P./Nafion	Ratio of SO <sub>3</sub> <sup>-</sup> involved in the C.P. doping
(1) Fe(ClO <sub>4</sub> ) <sub>3</sub> 0.25 M	Pyrrole 0.1 M	0.1	C <sub>8.18</sub> H <sub>3.52</sub> N <sub>1.00</sub> S <sub>0.22</sub> Cl <sub>0.13</sub> Fe <sub>0.03</sub>	(Pyr) <sub>1</sub> (ClO <sub>4</sub> ) <sub>0.13</sub> (Nf-SO <sub>3</sub> ) <sub>0.22</sub> Fe <sub>0.03</sub> (H <sub>2</sub> O) <sub>0.26</sub>	0.27	0.28	0.59
(2) Fe(ClO <sub>4</sub> ) 0.7 M	Pyrrole 0.7 M	1	C <sub>10.84</sub> H <sub>5.60</sub> N <sub>1.00</sub> S <sub>0.36</sub> Cl <sub>0.20</sub> Fe <sub>0.10</sub>	(Pyr) <sub>1</sub> (ClO <sub>4</sub> ) <sub>0.2</sub> (Nf-SO <sub>3</sub> ) <sub>0.36</sub> Fe <sub>0.1</sub> (H <sub>2</sub> O) <sub>1.3</sub>	0.26	0.17	0.17
(3) K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 0.3 M	Aniline 0.1 M	10 <sup>-4</sup>	C <sub>17.97</sub> H <sub>5.23</sub> N <sub>1.00</sub> S <sub>0.63</sub>	(An) <sub>1</sub> (Nf-SO <sub>3</sub> ) <sub>0.63</sub> (H <sub>2</sub> O) <sub>0.11</sub>	<sup>b</sup>	0.14	<sup>b</sup>
(4) Fe(ClO <sub>4</sub> ) <sub>3</sub> 0.7 M	Aniline 0.1 M	3 × 10 <sup>-5</sup>	C <sub>19.11</sub> H <sub>7.40</sub> N <sub>1.00</sub> S <sub>0.69</sub> Cl <sub>0.6</sub> Fe <sub>0.13</sub>	(An) <sub>1</sub> (ClO <sub>4</sub> ) <sub>0.0</sub> (Nf-SO <sub>3</sub> ) <sub>0.69</sub> Fe <sub>0.13</sub> (H <sub>2</sub> O) <sub>1.2</sub>	0.30	0.12	0.43
(5) Cu(ClO <sub>4</sub> ) <sub>3</sub> 0.7 M	Pyrrole 0.2 M	3 × 10 <sup>-7</sup>	C <sub>39.5</sub> H <sub>19.0</sub> N <sub>1.0</sub> S <sub>1.87</sub> Cl <sub>0.01</sub> Cu <sub>0.63</sub>	(Pyr) <sub>1</sub> (ClO <sub>4</sub> ) <sub>0.01</sub> (Nf-SO <sub>3</sub> ) <sub>1.87</sub> Cu <sub>0.63</sub> (H <sub>2</sub> O) <sub>8</sub>	<sup>b</sup>	0.03	<sup>b</sup>

<sup>a</sup> Nitrogen coefficient arbitrarily set to 1.00. <sup>b</sup> In these cases the level of protons cannot be accurately determined since the oxygen content was not given by the analytical technique, thus impeding a precise determination of the C.P. doping level.

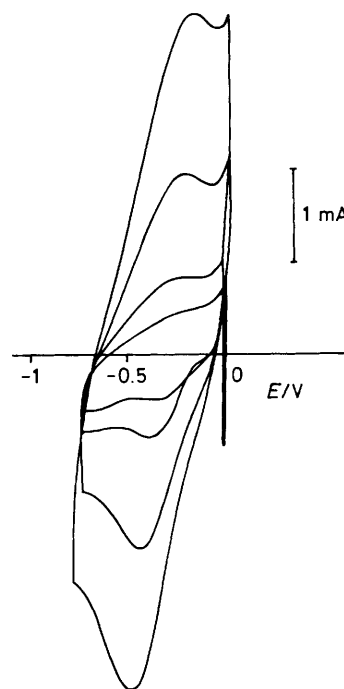
by stepwise diffusion of the appropriate oxidizer and of the aromatic substrate in the ionomer. Soaking an acidic Nafion® film in an aqueous solution containing 2 M Fe(ClO<sub>4</sub>)<sub>3</sub> and 0.5 M HClO<sub>4</sub> results in exchanging the proton sites of the Nafion® by iron(III) ions. Polymerization of aniline inside the ionic membrane is then obtained by soaking the Fe<sup>3+</sup> exchanged Nafion® in a 1 M aqueous solution of aniline acidified with H<sub>2</sub>SO<sub>4</sub> or HClO<sub>4</sub> (1.2 M); the membrane quickly turns deep green. However, after this operation it may be considered that only 1 in 21 ionic SO<sub>3</sub><sup>-</sup> sites of the ionomer is associated with the oxidized polyaniline cation since the other sites are associated with the protons and the Fe<sup>2+</sup> ions formed during the polymerization (equation 1), the Fe<sup>2+</sup>/Fe<sup>3+</sup> couple leading to one positive charge per 3 aromatic units.



An = aniline

The reaction sequence (Fe<sup>3+</sup> exchange/polymerization) can be repeated several times to increase the fraction of ionic sites exchanged against polyaniline. After seven iterations, the measured electronic conductivity is around 10 S cm<sup>-1</sup>. A similar experiment made with a 1 M pyrrole solution in acetonitrile and the same oxidizer solution leads to a polypyrrole-Nafion® M.C.P. exhibiting a comparable electronic conductivity.

With a more elaborate approach, instead of the successive dippings, a continuous growth of the polyaromatic polymer is obtained inside the Nafion® film by using the membrane to separate aqueous solutions of oxidizer and monomer. In these experiments large differences in electronic conductivity are observed between the two faces of the Nafion® membrane. Such differences arise from the preferential growth of the conducting polyaromatic polymer on the side in contact with the monomer solution. Electronic conductivity measurements with a four-probe system show that the M.C.P. is conducting or semi-conducting on the monomer face and insulating on the other face. Results of these experiments are summarized in Table 1. Analytical results are always calculated for one

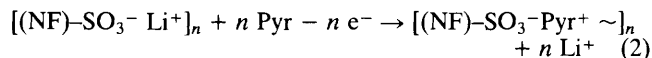


**Figure 1.** Cyclic voltammetry of a Nafion® doped polypyrrole film in a Nafion® 117 electrolyte (ca. 0.15 M in SO<sub>3</sub><sup>-</sup> ions) at scan rates of 10, 20, 50, and 100 mV s<sup>-1</sup>. Film synthesis is achieved by eight sweeps at 100 mV s<sup>-1</sup>, between -0.8 and +0.8 V in a 10<sup>-2</sup> M solution of pyrrole in the same electrolyte. The charge passed is 0.15 C cm<sup>-2</sup>.

pyrrole or aniline moiety and supposing that no loss of nitrogen takes place. In cases 1, 2, and 4, since an excess of Fe(ClO<sub>4</sub>)<sub>3</sub> is used, it is assumed that no H<sup>+</sup> remains inside the M.C.P. structure after washing, so that the doping level of the conducting polymer incorporated can be calculated as shown in Table 1. In the two remaining cases, however, such a hypothesis does not seem valid owing to the probable coexistence of H<sup>+</sup> (case 3) and leads to an apparent abnormal doping level value (case 5). The interest in using Fe(ClO<sub>4</sub>)<sub>3</sub> as

oxidizer lies in the complexing action of Fe<sup>III</sup> toward the ionic SO<sub>3</sub><sup>-</sup>-(NF) (NF = Nafion perfluorinated chains) sites which are not involved in the doping of the ionic conductive polymer matrix.

We have also prepared Nafion<sup>®</sup> doped polypyrrole films starting from aqueous Nafion<sup>®</sup> 117 solutions.<sup>†</sup> It is possible to grow such films on a platinum electrode by controlled or scanning potential electrolysis from an alcohol-free aqueous solution containing 0.01–0.1 M of pyrrole and 135 g/l of Nafion<sup>®</sup> 117 as supporting electrolyte. The electrochemical cell has previously been described<sup>5</sup> and the film growth is controlled by coulometry according to the polymerization reaction shown in equation (2).<sup>4</sup> A similar study was reported



by Fan *et al.*<sup>4</sup> In the present work we carefully got rid of all traces of ethanol from the ionomer solutions,<sup>†</sup> therefore

<sup>†</sup> Dissolution of 117 commercial Nafion<sup>®</sup> membrane into a mixture of water and alcohols by a few hours heating around 250 °C is a known procedure (W. G. Grot and F. Chadds, Eur. Pat., 0066 369, 1982, and C. R. Martin, T. A. Rhoades, and J. A. Ferguson, *Anal. Chem.*, 1982, **54**, 1639). Lithium exchanged membrane is used; by-products such as diethyl ether, as well as residual ethanol, are completely removed by controlled evaporation around 80 °C whilst small amounts of pure water are progressively added.

making sure that no ethanol oxidation would take place and perturb either the film synthesis or the cycling. Thin films of such a polymer can be cycled repetitively, even at high sweep rates, using the same Nafion<sup>®</sup> solution as supporting electrolyte (Figure 1). Peak currents scale linearly with the sweep rate as expected for a thin layer adsorbed species; this differs from Fan's results where a diffusion-controlled process is observed. Since ionomer chains are highly entangled within the polypyrrole structure, lithium cations are the only free-moving species. It can therefore be concluded that there is a fast Li<sup>+</sup> motion in and out of the film during the electrochemical process, and thus that a good conductivity is maintained in the film. Thick polymer films can be peeled off the electrode and handled when they are free-standing. After drying in vacuum they show an electronic conductivity of about 1 S cm<sup>-1</sup>.

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