

Ionic Liquid Electrolytes: A Potential Window of Enormous Opportunity

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Ionic liquid electrolytes present a number of advantages over conventionally used compositions in that they are non-volatile, generally have high ionic conductivity and can possess wide electrochemical potential windows. These attributes, combined with the diverse array of chemical functionalities that can be accommodated, have generated considerable interest among electrochemists. Of particular interest to us has been the electrochemical behaviour of chiral conducting polymers in a range of ionic liquids.

Chiral polyaniline doped with (+)- or (-)-10-camphorsulfonic acid (HCSA) can be prepared via the oxidation of aniline in the presence of aqueous (+)- or (-)-HCSA (1) or by the acid-doping of emeraldine base (EB) with (+)- or (-)-HCSA (2,3) in organic solvents. The use of these conducting polymers as chiral materials for chiral separations and for electrochemical asymmetric synthesis has been proposed. For electrochemical asymmetric synthesis of organic compounds, non-aqueous systems are required in order to solubilise the organic reactants and to provide a wide electrochemical potential window wherein the polymer and the electrolyte are stable. Room-temperature ionic liquids (ILs) present some interesting properties in this regard (4-6). The present paper reveals that the electrochemical stability of chiral polyanilines and their ability to retain their polymer chain conformation are highly dependent on the composition of the ionic liquid used.

Electrochemical Studies: the electrochemical behavior of PAn.(+)-HCSA films was explored using cyclic voltammetry in a variety of ionic liquids. Two well-defined redox couples (7), attributed to the conversion of leucoemeraldine \leftrightarrow emeraldine \leftrightarrow pernigraniline, were observed when PAn.(+)-HCSA films were cycled in ILs between ca. -0.2 and 1.2 V. Gradual changes in the CVs were observed over the initial 20-40 cycles before reaching a steady state. The electroactivity of the PAn.(+)-HCSA films could then be maintained for hundreds of cycles with only slight changes in the CV. When the potential range was extended to more negative potentials (-1.5 to -2.0 V), the electroactivity of the films exhibited good stability in the chiral IL [Ph(Me)NH₂Et⁺][TFSI⁻], recently synthesized (8) in our laboratories, (Figure 1a). In contrast, when scanned over this extended potential range the films lost electroactivity in the ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI, Figure 1b), 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF₆) and BMI-BF₄. However, the redox activity of the films was restored when subsequently scanned in aqueous acid.

When the potential range was extended to high positive potentials (+2.0 V) in EMI-TFSI and chiral (-)- α -methylbenzylethylamine-TFSI [Ph(Me)NH₂Et⁺][TFSI⁻], the films rapidly degraded and dissolved. Surprisingly, PAn.(+)-HCSA films exhibited excellent stability in BMI-

PF₆ over this extended positive range, but in BMI-BF₄ decreased with time. However, even in this latter case, after placing in aqueous acid a good CV was obtained without evidence of a middle oxidation peak associated with degradation of polyaniline (7, 9).

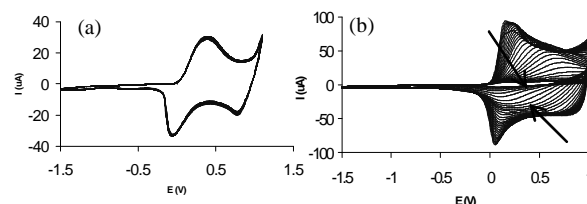


Figure 1. CVs of PAn.(+)-HCSA deposited on GC carried out in (a) [Ph(Me)NH₂Et⁺][TFSI⁻] for 20 cycles at 25 mV/s; (b) EMI-TFSI, 40 cycles at 50 mV/s.

Spectroscopic Studies: *In situ* UV-visible and CD spectra of PAn.(+)-HCSA films deposited on platinised ITO-coated glass electrodes were measured after exposure to a wide range of electrochemical conditions. When the films were held between -0.5 and -2.0 V, a strong absorption band appeared at ca. 320 nm attributed to leucoemeraldine base. No CD signal was observed when the films were reduced in BMI-BF₄. Similar behavior was observed in BMI-PF₆ and EMI-TFSI. This behavior contrasts with that of PAn.(+)-HCSA films when chemically or electrochemically reduced in aqueous media, where the optical activity of the films was retained. This difference may be due to cation movement into the polyaniline film during reduction in ILs (10). Fortunately, the undesirable racemization did not occur when the electrochemical reduction was carried out in [Ph(Me)NH₂Et⁺][TFSI⁻], since a strong bisignate CD signal was observed for the leucoemeraldine base.

These studies have laid the foundation for the development of a novel and efficient approach to electrochemical asymmetric synthesis.

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