E1- 10: Electrochemical behaviour and conductivity variation of polypyrrole prepared in aqueous NaCl

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Within the rapidly expanding field of polymeric conductors, highly conjugated polymers, such as polyacetylene (PA), polypyrrole (PPy), polythiophene (PTh), polyniline (PANI) and poly (p-phenylene vinylene) have

been attractive with respect of both scientific and industrial aspects in the past few years. In particular, they are of interest and the subject of intensive research because of their highly functional properties, which can be used in novel applications such as rechargeable batteries, electrochromic displays, smart windows, sensors etc. Among these, polypyrrole may be readily produced by electrochemical procedures, and has good environmental stability and relatively high electrical conductivity, and also it can be electrochemically synthesized from both aqueous and organic electrolytes using a broad range of dopant anions. The polypyrrole formed is highly conducting and can be electrochemically synthesized between conducting and insulating states in the same electrolyte or a different electrolyte, than that used in the electro-synthesis.

In this study polypyrrole films were galvanostatically electropolymerized from the monomer pyrrole in aqueous solutions of NaCl and their electrochemical behaviour and electrical conductivity variation were investigated.

Monomer pyrrole (Merck, Sur synthesis) was purfied by distillation prior to use. Salts employed NaCl, $NaClO_4$, CH_3COONa, NaH_2PO_4 and Na_2SO_4 were dried at 150°C for 45 h and 0.5 M electrolytes were prepared using doubly distilled water.

A standard 2 compartment 3 electrode electrochemical cell was used for the synthesis. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum gauze of large surface area. Electropolymerizations were carried out galvanostatically on platinum wires (1 cm long and 0.5 mm diameter) or on ITO glasses in a solution containing 0.1 M pyrrole monomer and 0.5 M electrolyte with current density of 64 $\mu A/cm^2$. For the conductivity studies the films were deposited on specially constructed 2 band micro electrodes.

After deposition, the polymer films were rinsed thoroughly with respective monomer-free electrolyte. Cyclic voltametry was carried out in the respective monomer-free electrolytes using a computer controlled potentiostat. Optical absorption spectroscopy in the range 320-1200 nm at various doping potentials was carried out using the films coated on ITO glass as one window

of a Teflon cell. Film resistance was measured using the PPy coated double band micro electrode which was immersed in the electrolyte and the potential was held at the desired value in the range from -0.9 to 0.4 V vs SCE using a DC power supply. The resistances of the films were computed from ac impedance measurements which were carried out in the frequency range from 10^5 to 0.1 Hz using a Solatron frequency response analyzer.

The film on Pt when mounted in an aqueous solution of NaCl, can be electrochemically switched between oxidized (conducting) form and the neutral (insulating) form. The cyclic voltamograms and the optical absorption spectra show that the reaction involves the oxidation of extended π-system of the polymer and produces a colour in the film from yellow when neutral to black when oxidized. The redox potential appears to be independent of scanning speed, and the relation between the peak current and the sweep rate in the range 10-100 mV/s was found to be linear. In this study the optical absorption spectra show that the band of neutral polypyrrole is 3.185 eV. In our previous studies based on dry organic solvents, the band gap determined for highly conjugated PPy was 2.83 eV compared to 3.2 eV for a form with low conjugation. The shape of the voltamograms in $NaCl/H_2O$ are more like the curves which were obtained from low conjugated films in organic solvents. Therefore comparing these results it can be concluded that films formed in aqueous solution of NaCl have a lower conjugation length than films formed in non aqueous solutions.

As seen in the *in-situ* conductivity studies on PPy, the film resistance decreases with increasing potential (doping level) exponentially in the voltage range from 0.9 to 0.4 V vs SEC.

The effect of the pH of the polymerization solution on the electrochemical properties of PPy was studied, and it was found that PPy preparation solutions with pH 2 had the highest capacity. Furthermore the effect of the anion present during doping was investigated by cycling PPy in solutions containing Cl^-, ClO_4^-, CH_3COO^-, $H_2PO_4^-$, and SO_4^{2-}.

The PPy films formed in aqueous solutions of NaCl have a lower conjugation than films formed in non aqueous solutions. Better films are obtained when prepared in solutions with pH 2. The resistance of the films decreases exponentially with increasing potential in the voltage range from -0.9 to 0.4V vs SCE.