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**STUDIES ON SELECTED CONJUGATED CONDUCTING
POLYMERS, POLYMER ELECTROLYTES AND
INORGANIC ELECTROLYTES**

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Studies On Selected Conjugated Conducting Polymers, Polymer Electrolytes and Inorganic Electrolytes

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Abstract

The influence of the polymerization conditions on properties of electrochemically synthesized polypyrrole (PPy) films were studied with the aim of preparing high quality, highly stable and reproducible films. The electroactivity, conductivity and morphology were examined, by using Cyclic Voltammetry, *In-situ* UV-Visible Optical Absorption Spectroscopy, *In-situ* A.C Impedance Spectroscopy, XRD, SEM and ESR techniques. A systematic investigations of the influence of the current density during polymerization on the properties of PPy have been carried out either in non-aqueous electrolytes or aqueous electrolytes. With the dry non-aqueous electrolytes, low current density is crucial for the formation of a highly conjugated modification as shown by the lowest value reported so far for the π - π^* transition energy, 2.83 eV. Two types of PPy films can be identified, low current density form ($I/A \leq 300 \mu\text{A cm}^{-2}$), and the high current density form ($I/A \geq 500 \mu\text{A cm}^{-2}$) with the dry electrolytes. The limiting modifications are obtained when using $I/A \leq 60$ and $I/A \geq 2000 \mu\text{A cm}^{-2}$, respectively. The π - π^* transition is shifted to higher energies in the high current density films (3.1 eV).

The films formed at low current densities have a grater stability than those polymerized at high current densities. Water present in the solvents during polymerization leads to the formation of PPy films with low stability and low conductivity.

It is seen that from the studies based on the solvent/solute effects, there is no "memory effect" with respect to the solvent used during film formation. Change of the electrolytic anion showed that the polymer may have some "memory" of the shape or size of the anion present during formation.

The kinetics of insertion of perchlorate ions into PPy is investigated by electrochemical impedance spectroscopy. The electrical conductivity of the PPy films seemed to depend upon the structure of the counter ions. The surface morphology, adhesion to the substrate and the crystallinity of the polypyrrole films are enhanced in the low current density form.

ESR results on the PPy films indicate that the bipolarons to be the dominant charge carrier in highly conjugated films low current density films. However, in the high current density films, with lower conjugation, the polarons seem to be more stable and contribute to the conduction process.

In the aqueous electrolytes it is difficult to obtain distinct low current density and high current density forms. At very low current densities the polymerization was found to be poor.

The study on proton conducting poly(ethylene imine) with phosphoric acid polymeric system, indicates that the conductivity can be enhanced by the addition of highly dispersed silica (fumed silica).

Some inorganic solid electrolyte systems were also studied. A range of stable solid solutions with γ -LISICON type structures, were formed in the system $\text{Li}_{4-2x}\text{Ge}_{1-x}\text{S}_x\text{O}_4$ ($0.08 < x < 0.42$). This phase has high Lithium ion conductivity with a maximum value (bulk) of $\sim 1.85 \times 10^{-5} \text{ S cm}^{-1}$ for $x = 0.20$ at 27°C .

The ternary composition corresponding to $\text{Li}_{0.22}\text{Na}_{1.33}\text{Zn}_{0.22}\text{SO}_4$ incooperated in solid state cells with configurations Zn/electrolyte/ MnO_2 and Zn/electrolyte/Cu and their discharge characteristics have been investigated at 350°C . The Zn/ MnO_2 configuration gives an open circuit voltage of $\sim 1.2 \text{ V}$, a short circuit current of $\sim 1.4 \text{ mA}$ and a capacity $\sim 0.3 \text{ mA h}$. For Zn/Cu configuration the corresponding values are 1.0 V , 15 mA and $\sim 2 \text{ mA h}$.

