

C 541.3
VID

**POLYPYRROLE BASED CONDUCTING POLYMERS AND THEIR
ELECTROCHEMOMECHANICAL PROPERTIES**

A THESIS PRESENTED

BY

KAMAL PUSHPAKUMARA VIDANAPATHIRANA

to the

POST GRADUATE INSTITUTE OF SCIENCE

in partial fulfillment of the requirement

for the award of the degree of

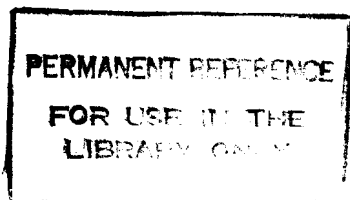
DOCTOR OF PHILOSOPHY

of the

UNIVERSITY OF PERADENIYA

SRI LANKA

March 2000



539753

**POLYPYRROLE BASED CONDUCTING POLYMERS AND THEIR
ELECTROCHEMOMECHANICAL PROPERTIES**

K. P. Vidanapathirana

Department of Physics
University of Peradeniya
Peradeniya
Sri Lanka

Board of study: Physics

Degree: Ph. D.

The influence of preparation conditions on the properties of electroactive poly-N-methylpyrrole (PNMP) films were investigated with the view of obtaining highly conductive films. PNMP films were galvanostatically polymerized in aqueous electrolytes by varying the electrolyte concentration, current density, type of doping anion, pH of the electrolyte and the polymerization temperature. The films obtained were characterized using cyclic voltammetry and impedance spectroscopy. Conductivity of PNMP films was very much affected by the polymerization current density, pH and the polymerization temperature whereas no considerable effect was observed when the concentration of the electrolyte and the size of the anion were changed. Highest conductivity for PNMP films (43 mS cm^{-2}) was obtained with the following conditions: electrolyte concentration = 0.5 M, current density = $62.5 \text{ } \mu\text{A cm}^{-2}$, anion = ClO_4^- , pH = 1.0 and polymerization temperature = $3 \text{ } ^\circ\text{C}$.

Mass changes occurring in PNMP films during the redox process due to ion exchange were investigated using an Electrochemical Quartz Crystal Microbalance (EQCM). The mass changes and dependence of peak potentials of cyclic voltammograms

(CVs) with respect to cycling electrolyte concentration revealed that anions are the moving species during the redox process in PNMP films that were prepared and cycled in aqueous electrolytes containing small anions.

Polypyrrole (PPy) films were prepared with large surfactant anion, dodecyl benzenesulfonate (DBS⁻), and their properties were compared with those of PPy films prepared with small anions under similar conditions. It has been observed that the stability of PPy/DBS films made in aqueous electrolytes was same as that of the PPy films made in non aqueous electrolytes.

EQCM studies and dependence of peak potentials of CVs on cycling electrolyte concentration of PPy/DBS films showed a dual step scheme for the redox process in the films when they are cycled in aqueous electrolytes. During oxidation, cation expulsion takes place at lower potentials whereas anion insertion takes place at higher potentials. During reduction, anion expulsion at higher potentials and cation insertion at lower potentials takes place.

Lithium rechargeable cells were fabricated using PPy/DBS as the cathode and polyacrylonitrile (PAN) based electrolyte as the separator. These cells were characterized by cyclic voltammetry, impedance spectroscopy and continuous charge-discharge cycling. Kinetics of these cells seemed to be governed by ion diffusion. Continuous charge-discharge experiments showed that these cells could be cycled more than 1000 times without any appreciable charge decay.

Electrochemomechanical properties of PPy/DBS films were investigated by fabricating bi-layer and dry artificial muscles and obtaining the force exerted by these muscles and the cyclic voltammograms simultaneously. The highest change in the force

can always be associated with the main peaks of the cyclic voltammogram. It has been observed that appreciable force change occurred in a rather narrow voltage interval. Muscles fabricated with PPy films prepared using larger anions and higher polymerization current densities gave higher forces. Higher forces can also be obtained by limiting the cycling potential window so that only cation exchange occurs.

PERMANENT REFERENCE
FOR THE NAME
LIBRARY