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Electrolyte Dependence of Charge Injection Processes  
for Electroactive Polymer Films

by

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## Electrolyte Dependence of Charge Injection Processes for Electroactive Polymer Films

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Differences in cyclic voltammetric behavior when using acetonitrile as an electrolyte solvent as compared to water solutions have been reported for redox polymers such as poly(vinylferrocene) (PVF)<sub>2</sub>. These differences are attributed to the degree of solvent uptake into the polymer film, activity of anion in the solvent, changes in site-site interaction parameters for the polymer film, and differences in the reduction wave deswelling process (see figure 1). Solvents penetrate glassy polymers and induce backbone motions of the polymer fibril. In the presence of any low molecular weight liquid, the polymer is swollen, and the free volume increases. The free volume may also change as the result of electrochemical cycling between the neutral and oxidized form of PVF. Reversibility of the charge-injection process for these films varies with the salt and choice of solvent. Cyclic voltammetry and quartz crystal microbalance (QCM) studies of NaCF<sub>3</sub>SO<sub>3</sub> and NaPF<sub>6</sub> in acetonitrile show irreversible degradation of PVF with charge capacity decreasing with each cycle and no net increase in mass (see figure 2). The same anions exhibit excellent reversibility in water solutions.

PVF films have been studied recently by impedance techniques (6), and were found to have three regions of behavior characterized by different relaxation times. At high frequencies, the simultaneous injection of holes (oxidation of the ferrocene pendant groups) and anions (to maintain charge neutrality) is the rate-controlling process (kinetic control). At intermediate frequencies, diffusion (of anions and holes) in the film is rate-limiting. At the lowest frequencies, the finite thickness of the films cause the impedance to become purely capacitive (charge saturation). The latter region has been termed the redox capacity region of impedance.

AC impedance analysis gives quantitative information about the charge-injection process. For the highly reversible system of LiClO<sub>4</sub> in acetonitrile, no change in the three characteristic regions (kinetic control, diffusion control, charge saturation) was observed during cycling. For non-reversible systems of NaCF<sub>3</sub>SO<sub>3</sub> and NaPF<sub>6</sub> in acetonitrile, consecutive cycles should produce an increase in the charge transfer resistance (high-frequency semicircle) and a decrease in the overall redox capacity (low frequency capacitive region). Impedance analysis of PVF cycling in these salts will be presented.

An examination of the degree of electrolyte inclusion during break-in of dry (spin-coated) PVF films is possible with the use of QCM and Phase Detection Interferometric Microscopy (PDIM). Effects of changes in electrolyte concentration, associated cation and solvent will be discussed for redox films such as PVF.

## Acknowledgement

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POLYVINYLFERROCENE/ CYCLIC VOLTAMMOGRAMS

COMPARISON OF WATER VS. ACETONITRILE

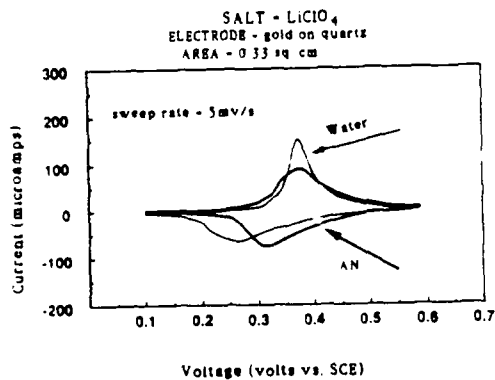


Figure 1. Cyclic voltammetric behavior of PVF in solutions of 0.1 M  $\text{LiClO}_4$  in acetonitrile and water.

Polyvinylferrocene  
 $\text{NaCF}_3\text{SO}_3$  in AN

Capacitive Loss During Cycling

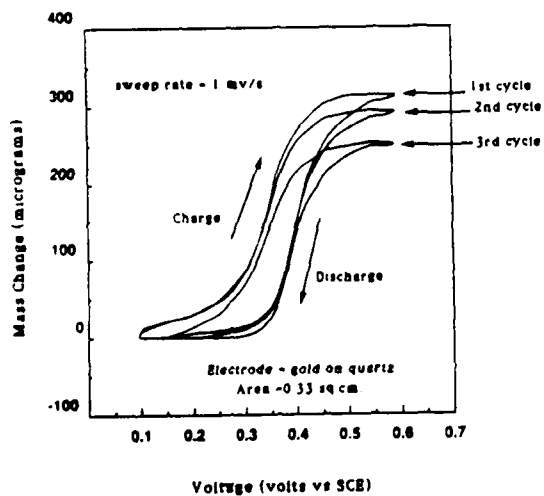


Figure 2. Mass change of PVF films in 0.05M  $\text{NaCF}_3\text{SO}_3$  in acetonitrile as solvent.