

Solvent-Dependent Electrochemical Behavior of Polyaniline

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Polyaniline is one of electroactive conducting polymers which have been continuously the subject of a great number of researchers. In view of various applications of polyaniline such as rechargeable batteries, electrochromic displays, electrocatalysts, etc, considerable research attention has been called to the electrochemistry of polyaniline, since its chemical and physical properties are strongly dependent on the transition between the oxidized and reduced forms of polyaniline. It has been long recognized that the electrochemistry of polyaniline is strongly affected by acidity of solutions in which polyaniline films are soaked.

We have recently reported that polyaniline shows electrocatalytic activity toward sluggish electron-transfer reactions of organosulfur compounds which are expected as a candidate for high energy cathode material for polymer lithium batteries¹⁾. Since electrocatalytic activity of polyaniline is based on facile electron-transfers between polyaniline and organosulfur compounds. We expect that detailed studies on the electrochemistry would lead to the improvement of polyaniline electrocatalysis and thus development of organosulfur-based cathode materials for high energy lithium batteries of practical use.

In this study, we examined electrochemical behavior of polyaniline and its model compound, *N,N'*-diphenyl-*p*-phenylenediamine (DPPD, reduced form) and *N,N'*-diphenyl-*p*-benzoquinoneimine (QDIM, oxidized form) in organic solvents with different basicity.

Polyaniline films coated on glassy carbon electrodes show reversible redox responses in propylene carbonate (PC) which is frequently used as an electrolyte in lithium batteries. When *N*-methyl-2-pyrrolidinone (NMP) was added to a PC solution, shift in the peak potentials and decreases in the redox currents were observed. Adding a protonic acid such as trifluoroacetic acid to PC solutions containing NMP, the diminished redox activities of polyaniline films were recovered to almost original magnitude. Therefore, the loss of electroactivity of polyaniline films was due to the loss of protons from the imine nitrogens of the oxidized polyaniline.

Spectroelectrochemical experiments were also carried out to further study electrochemical reactions of polyaniline films in different organic solvents. It was concluded based on potential-dependent absorption spectra of polyaniline films that the addition of NMP to PC solutions induced proton loss at most oxidized form, pernigraniline.

Polyaniline model compounds, DPPD and

QDIM, were similarly examined in this study to examine solvent-dependent electrochemistry of polyaniline in more detail. The model compound DPPD showed clearly solvent-dependent electrochemical responses. The cyclic voltammogram of DPPD showed two, well-defined reversible redox couples in PC. On the contrary in NMP, an irreversible redox response was obtained. Spectroelectrochemical experiments confirmed the proton loss from QDIM which is two-electron oxidation form of DPPD and a model compound for pernigraniline.

REFERENCES

- 1) N. Oyama, T. Tatsuma, T. Sato and T. Sotomura, *Nature (London)*, **373**, 598 (1995).