

Polypyrrole Derivatives Covalently Attached with Sulfur-Containing Groups

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In the last two decades, chemical derivatization of conducting polymers have been extensively conducted in seek for novel or improved functions for energy storage systems, sensors, electrochromic displays and electrocatalysis. Among conducting polymers, polypyrrole derivatives have attracted certain interest, because of the ease of molecular modification of pyrrole monomer in addition to versatility inherent to polypyrrole.^{1,2)} A wide variety of pyrrole monomers have been synthesized and electrochemical polymerization of those monomers have lead to polypyrrole-modified electrodes with various functions.

In this study we synthesized a series of mono- and di-substituted pyrrole monomers which possess sulfur-containing substituents at 3-position and 3- and 4-positions, respectively.³⁾ Several alkylthiol-substituted pyrrole monomers have been prepared to form self-assembled monolayers (SAM) on noble metal electrode surfaces through a S-Au bond.⁴⁾ In this study, on the other hand, our attention is mainly focused on the chemically reversible redox conversion between thiol and disulfide on polypyrrole chains.⁵⁾ We expect covalently attaching thiol groups onto polypyrrole would accelerate sluggish kinetics of thiol redox reactions due to electrocatalytic activity of polypyrrole.

Substituted pyrrole monomers examined in this study were prepared from an *N*-blocked pyrrole monomer.⁶⁾ Structures of the monomers were confirmed by NMR and IR. The monomers were electrochemically polymerized on carbon electrodes and electrochemistry of the resulting polypyrrole films were examined by cyclic voltammetry and quartz crystal microbalance method, in combination with spectroscopic methods.

The sulfur-containing pyrrole monomers synthesized in this study were oxidized at electrode surfaces to give polypyrrole films on electrode surfaces. Oxidation potentials of the monomers and redox activity and potentials of the resulting polymers were largely dependent on the sulfur-containing substituents on pyrrole monomer. Generally, the redox reactions of the substituted polypyrroles prepared in this study were observed at a more positive potential region compared to unsubstituted polypyrrole. A mono-substituted polypyrrole, for example poly(3-thiomethylpyrrole), gave high redox activity. However, there obtained no evidences for the thiol-disulfide redox conversion on the polymer chain. That is, the observed high redox activity of poly(3-thiomethylpyrrole) mainly comes from polypyrrole chain. QCM studies suggested the redox reaction of the film was accompanied by an anion movement to maintain electroneutrality in the film.

Poly(3,4-dithiomethylpyrrole), one of the disubstituted polypyrroles, gave redox activity which was much smaller than that of unsubstituted polypyrrole. On

the contrary, another disubstituted polypyrrole derivative showed enhanced electroactivity, implying the sulfur-containing groups introduced onto polypyrrole chains being electroactive due to electrocatalytic activity of polypyrrole. It was also found that the redox activity and surface morphology of the highly active polypyrrole derivative were dependent on electrolytes used in electrochemical polymerization.

These novel polypyrrole derivatives modified with electroactive sulfur-containing groups are expected highly promising as a high energy cathode material for polymer lithium batteries.

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