Effects of Cresol-Sulfonic Acid on Redox Behavior of Polyaniline

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Polyaniline was possibly doped with cresol-sulfonic acid, though it failed to electrodeposit the polymer from solutions of aniline in cresol-sulfonic acid. The presence of cresol-sulfonate anions changed the redox peaks of the polymer in their positions and heights. Catalytic oxidation of cresol-sulfonic acid was observed on polyaniline-filmed electrodes at potentials of a limited interval.

The redox processes of polyaniline have been extensively studied with various methods. The redox behavior of polyaniline is affected by a number of factors such as the pH of solution,[1] and the nature of acid anions.[2] The redox processes of polyaniline make an important contribution to the electrocatalytic effects of the polymer as an electrode material on many redox reactions, especially for the electrooxidation of some organic compounds.[3] Joeseph and Trivedi reported that the oxidation of *o*-cresol at pH 9 on polyaniline-filmed stainless-steel electrodes resulted in deposition of a porous film of poly(*o*-methylphenoxyphenylene).[3] MacDiarmid and Epstein [4] have recently reported a phenomenon of secondary doping of polyaniline. They have found that a secondary dopant (an apparently "inlet" substance, such as *m*-cresol) induces still further increase in conductivity of the polyaniline doped with a primary dopant (such as *d,l*-camphorsulfonic acid). [4] Cresol-sulfonic acid has both a nature of sulfonic acids and a basic molecular structure of a secondary dopant *m*-cresol. It seems interesting to dope polyaniline with cresol-sulfonic acid in view of increasing the conductivity of polyaniline. In the present work, we reported some preliminary results on the redox behavior of polyaniline and its doping in solutions of cresol-sulfonic acid, and the catalytic oxidation of cresol-sulfonic acid on polyaniline-filmed electrodes.

All the experiments were carried out at 25 °C under an inert atmosphere in a conventional three-electrode cell with a 0.1 cm Pt disc electrode. All the potential were reported versus a saturated calomel electrode. The polyaniline-filmed electrodes were obtained from a solution of 0.25 M aniline in 0.5 M H_2SO_4 (1 M = 1 mol dm^{-3}) at a constant current density of 1 mA cm^{-2} by passing an anodic charge of 100 mC cm^{-2} for polymerization.

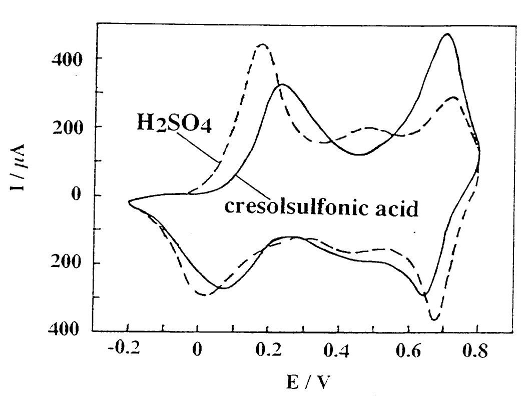

Figure 1. Voltammograms (100 mV s^{-1}) of a polyaniline film in 0.5 M cresol-sulfonic acid (solid) and in 0.25 M H_2SO_4 (dotted).

Figure 1 shows voltammograms of the polyaniline film in 0.5 M cresol-sulfonic acid and 0.25 M H_2SO_4. Being consistent with the literature,[1] the polyaniline film in H_2SO_4 exhibits two pairs of main redox peaks and a pair of minor peaks (middle peaks). Within the same potential window, no evident redox peak was observed at a bare Pt electrode in 0.5 M cresol-sulfonic acid. However, the voltammogram of the polyaniline film in 0.5 M cresol-sulfonic acid is rather different from that in 0.25 M H_2SO_4. The middle oxidation peak for the polymer film in cresol-sulfonic acid seems to disappear, though its corresponding reduction peak remained. Moreover, an evident shift in the peak potentials for the first main redox pair in cresol-sulfonic acid was observed, along with a decrease in the peak current, with comparison to those in H_2SO_4. In contrast, the peak potential for the second main redox pair shifted negatively, along with an increase in the oxidation current in cresol-sulfonic acid. Similar effects were observed for polyaniline-filmed electrodes in 0.25 M H_2SO_4 with and without the presence of 0.1 M cresol-sulfonic acid.

The first oxidation peak involves a one-electron, one-proton loss at a pH less than 1, and it shifts linearly to anodic values at a rate of ca. 60 mV per pH unit in the pH range -1 to 1 at constant ionic strength.[1] The second main oxidation peak corresponds to a two-proton, one-electron oxidation. It is also dependent on pH and shifts by ca. -120 mV per pH unit in the pH range between 1 and 4.[5] The pH dependence of these two peaks cannot account for the shift in the peak potentials, because there is a similar shift in the redox peaks even by adding 0.4 M cresol-sulfonic acid into a solution of 0.2 M H_2SO_4, as shown in Figure 2. Thus, the shift of the peak potentials and the increase in the peak currents were possibly from the effect of the cresol-sulfonate anion. To our knowledge, the effect of anions on the

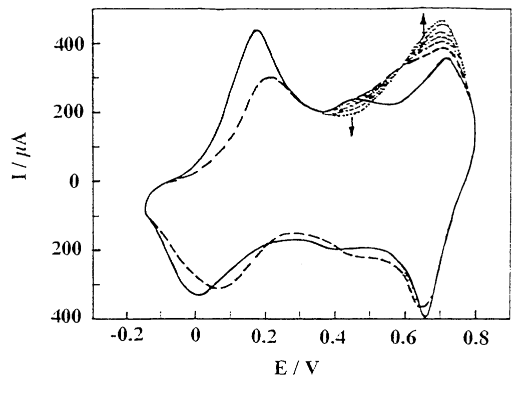

Figure 2. Voltammograms (100 mV s^{-1}) of a polyaniline film in a solution of 0.4 M cresol-sulfonic acid and 0.2 M H_2SO_4 (dotted) and in a solution of 0.2 M Na_2SO_4 and 0.2 M H_2SO_4 (solid). The arrows show the shifting of the curves for the third to the tenth cycles.

position and shape of the oxidation peaks for polyaniline have yet not reported in details, though both the egress of protons and ingress of anions have been suggested as a possible dynamic phenomena which accompany the redox reaction for the first main pair.[2] The shift in the peak potentials due to the addition of cresol-sulfonic acid is possibly related to a possible change in basicity of polyaniline due to the incorporation of cresol-sulfonate ions into the polymer film. In addition, we have recently suggested that a possible protonated-polyaniline-anion complex may take an important role in the electrosynthesis and overoxidation of polyaniline.[6] From the view of this point, it is not surprising that the presence of cresol-sulfonic acid in solutions of H_2SO_4 changes the position and height of the redox peaks for polyaniline. However, it needs further study to obtain a clearer relationship between the related parameters.

The middle oxidation peak was found to shift positively with the presence of cresol-sulfonic acid, depending on at least the concentration of cresol-sulfonic acid and the rate of potential sweeping. As shown in Figure 2, the middle oxidation peak was observed as a shoulder in a solution of cresol-sulfonic acid for the first several potential cycles. With the cycle number increased, the middle peak shifted to more anodic values, and finally overlapped with the second main oxidation peak. Hence, the steady-state voltammogram was similar in the shape to that shown in Figure 1 in a solution of cresol-sulfonic acid, where the middle oxidation peak seemed to disappear.

Several possible reactions have been assigned to account for the middle oxidation peak; one of them is due to the *p*-aminophenol/benzoquinone imine redox pair.[7] The dependence of the shift in the middle oxidation peak on the concentration of cresol-sulfonic acid and the scan rate suggested that in addition to the reaction from the polymer film itself, there was possibly another reaction due to the oxidation of cresol-sulfonic acid. The increase in the current around the second main oxidation peak in solutions of cresol-sulfonic acid hints that the polyaniline film electrode may catalyze the oxidation of cresol-sulfonic acid.

The steady-state oxidation of cresol-sulfonic acid was carried out on Pt and polyaniline-filmed Pt electrodes with or without the presence of H_2SO_4 as supporting electrolyte, parts of the results are shown in Figure 3. The reading of the oxidation current was obtained after the electrode was stepped to a given potential and held for 5 min, in order to eliminate the influences of the charging current and the oxidation current of the polymer itself. As shown in Figure 3, there is no evident oxidation current at a bare Pt electrode in solutions of cresol-sulfonic acid. However, reasonable oxidation currents are observed at a limited potential interval around the second main oxidation peak for polyaniline, even subtracting the background oxidation current at a polyaniline-filmed Pt electrode in the solutions without the presence of cresol-sulfonic acid (which is not given in Figure 3, but much lower than those with the presence of cresol-sulfonic acid). It is possibly due to the oxidation of cresol-sulfonic acid. The oxidation current did not change evidently when the concentration of cresol-sulfonic acid was increased, or when the oxidation was carried out in solutions of cresol-sulfonic acid without the presence of H_2SO_4 as supporting electrolyte. The polyaniline film becomes more stable in solutions containing cresol-sulfonic acid. After the polymer films were oxidized at 0.8 V for 10 min in solutions of 0.2 M H_2SO_4 and 0.2 M Na_2SO_4, and of 0.2 M H_2SO_4 and 0.4 M cresol-sulfonic acid, the coulombic capacity at the potential window from -0.1 V to 0.35 V for the first oxidation peak of polyaniline was decreased by 46.2% in the solution without the presence of cresol-sulfonic acid, while by 22.4% in the solution with the presence of cresol-sulfonic acid. Therefore, it is difficult to account for the decrease in the oxidation current of cresol-sulfonic acid with the aid of the possible oxidative decomposition of polyaniline. In fact, the retained oxidation currents beyond 0.8 V at polyaniline electrodes in solutions with the presence of cresol-sulfonic acid were higher than those without the presence of cresol-sulfonic acid. This catalytic oxidation reaction seems interesting in view of synthesis. The kinetics for the oxidation reaction need a further study.

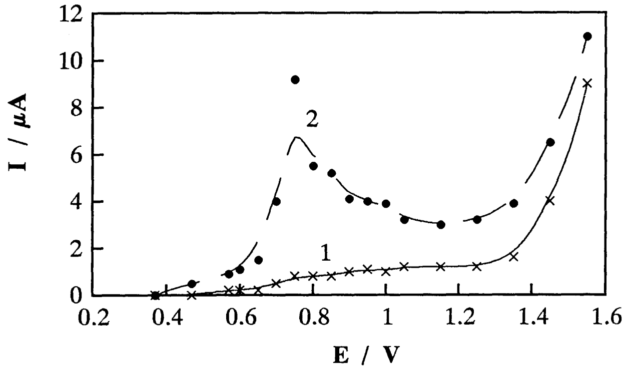

Figure 3. Steady-state oxidation of cresol-sulfonic acid (0.1 M) in 0.25 M H_2SO_4 at a bare Pt electrode (1) and a polyaniline-filmed Pt electrode (2).

We failed to electropolymerize aniline in cresol-sulfonic acid, though evident oxidation currents were observed beyond about 0.8 V for first several cycles of potential. The initial oxidation currents, rising from the oxidation of the monomer, decreases as the cycle number increased. The polymerization was yet impossible by increasing the applied potential (for a constant-potential electrolysis) or by increasing the potential upper limit (for an electropolymerization by successive potential cycling), though the initial oxidation currents were promoted. This is possibly due to the detrimental effect of the oxidation product of cresol-sulfonic acid on the stability of the radical cations of aniline, which is necessary for the polymer formation. However, the polyaniline prepared in a solution of a common acid can be doped with cresol-sulfonic acid by ion exchanging. After prepared at 0.8 V from a solution 0.25 M aniline in 0.5 M H_2SO_4, the polyaniline samples was dedoped and doped three times by holding the potential at -0.3 V and 0.5 V in turn for 10 min at each potential, in 0.25 M H_2SO_4 or in 0.5 M cresol-sulfonic acid. The cresol-sulfonic acid-doped sample shows a conductivity of 0.77 S cm^{-1}, while the H_2SO_4-doped sample 0.18 S cm^{-1} and the dedoped sample at the order of 10^{-3} S cm^{-1}.

References

1 J. C. Lacroix and A. F. Diaz, *J. Electrochem. Soc.*, **135**, 1457(1988).
2 C. Barbero, M. C. Miras, O. Haas, and R. Kötz, *J. Electrochem. Soc.*, **138**, 669(1991).
3 J. Joeseph and D. C. Trivedi, *Bull. Electrochem.*, **4**, 469(1988).
4 A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, **65**, 103(1994).
5 G. Inzelt and G. Horányi, *Electrochim. Acta*, **35**, 27(1990).
6 H. Tang, A. Kitani, and M. Shiotani, *Electrochim. Acta*, in press.
7 Y.-B. Shim, M.-S. Won, and S.-M. Park, *J. Electrochem. Soc.*, **137**, 538(1990).