

Electronic Control of pH at Sulfonated Polyaniline Electrodes

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Electrochemical modulation of self-doped sulfonated polyaniline is demonstrated to provide electronic control of pH and enzyme activity in the vicinity of the electrodes.

Electrochemical doping of conducting polymers consists of the electron- and ion-transfer processes in the polymer systems.¹⁻⁴ In this report, we demonstrate that proton transfer is involved in the first redox process of the self-doped conducting polymer, sulfonated polyaniline.⁵ Based on the experimental evidence a proton sponge (or a pH modulator) is proposed and its modulating speed and durability are examined.

Typical cyclic voltammograms of the first redox process in different pH solutions of a sulfonated polyaniline film cast on

Pt are shown in Fig. 1. In order to obtain direct evidence that the proton serves as the counter ion in this process we used a microcombination pH probe (Microelectrodes, Inc., MI-410) placed on the surface of the film electrode. The response time of the pH probe was less than 5 s. The result of an *in situ* pH determination during the first redox process is shown in Fig. 2. The response of the pH can be explained in the following redox mechanism of sulfonated polyaniline.

As the potential is increased, the sulfonated polyaniline film

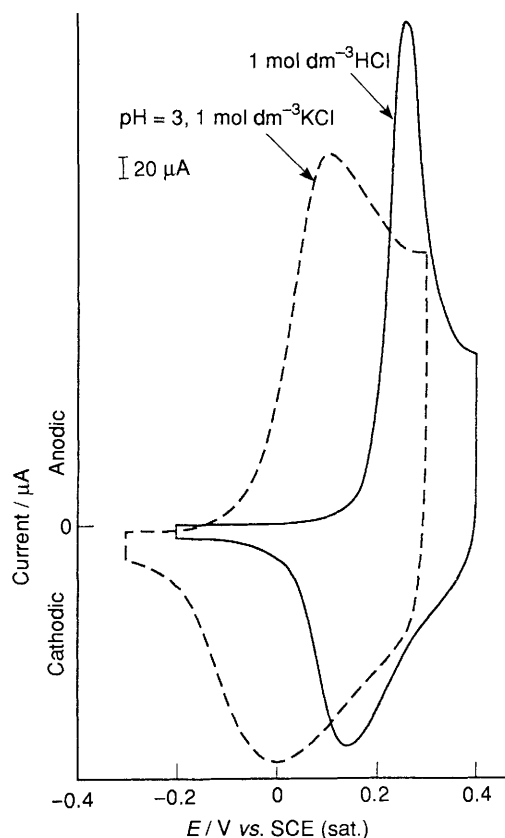
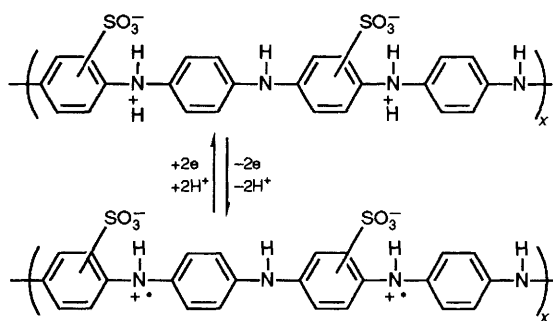


Fig. 1 Typical cyclic voltammograms (50 mV s^{-1}) of first redox process of sulfonated polyaniline, where the working electrode was a polymer coated Pt foil, the counter electrode was a Pt foil and the reference electrode was saturated calomel electrode in $1.0 \text{ mol dm}^{-3} \text{ HCl}$ (—) and pH 3, $1 \text{ mol dm}^{-3} \text{ KCl}$ solutions (---)

is oxidized to generate polarons in the polymer chain, and there is a resultant loss of protons. In this process ejection of electrons into the electronic circuitry from the polymer system is compensated for by the ejection of protons from moieties covalently bound to the polymer into the surrounding medium. As a result, the pH of the solution in the vicinity of the electrodes is decreased. After the reversal of the scan direction, the flow of cathodic current resulted in neutralization of polarons and absorption of protons, while the pH changes back to its original value. This redox process is an electron-proton transfer mechanism involving an equal number of electrons and protons and exhibits a variation of 59 mV pH^{-1} for the half-wave potential.⁶ The direct measurement of the pH change during modulation of the potential supports the mechanism proposed previously.⁶ In order to rule out the possibility of the pH change caused by reduction of oxygen in the aqueous solutions, we examined bare Pt and polyaniline coated Pt electrodes under the same experimental conditions and found no detectable change in pH. These observations clearly show that the pH change, which accom-

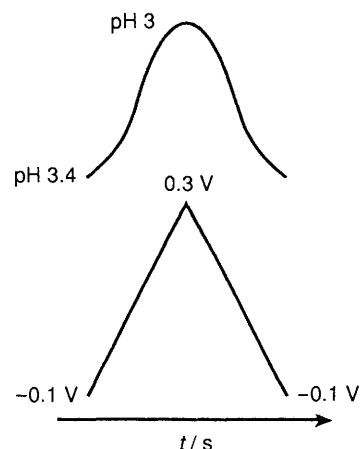


Fig. 2 The pH curve obtained simultaneously with a cyclic voltammogram of sulfonated polyaniline on a Pt electrode in $1.0 \text{ mol dm}^{-3} \text{ NaCl}$, pH 3 solution. Scan rate = 10 mV s^{-1}

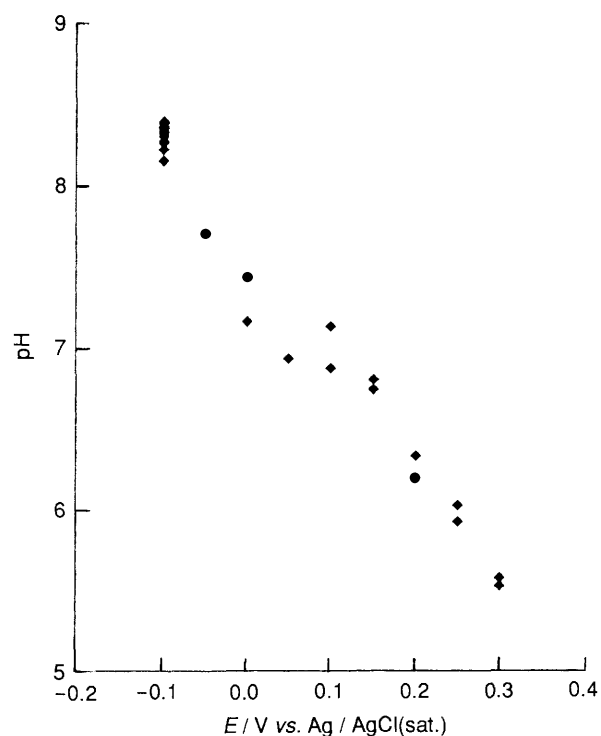


Fig. 3 The pH change in the vicinity of sulfonated polyaniline coated Pt electrode upon double step potential between -0.1 and 0.35 V vs. $\text{Ag/AgCl}(\text{sat.})$ in 1.0 mol dm^{-3} (pH 5.6) NaCl , the charge was of 0.2 mC

panies the redox process, tracks the reduction and oxidation of sulfonated polyaniline, and that the release and absorption of protons are reversible.

Fig. 3 shows the pH change near the surface of the film electrode caused by a step potential between -0.1 and 0.35 V vs. $\text{Ag/AgCl}(\text{sat.})$. A one to one correspondence between applied potential and pH is found. The magnitude of the pH change per volt is dependent on the pH of the electrolyte. For example, the pH change is 3.5 pH V^{-1} in $\text{pH} \sim 3$ solution while the change is 7.5 pH V^{-1} in $\text{pH} \sim 6$ electrolyte.

Sulfonated polyaniline is particularly durable for $\text{pH} \leq 4$ and potential lower than 0.35 V vs. $\text{Ag/AgCl}(\text{sat.})$. For example, the optical reflectance of a film on a Pt electrode changed less than 20% after 7 million cycles in $1 \text{ mol dm}^{-3} \text{ HCl}$.

The experimental results demonstrate that sulfonated polyaniline behaved as a proton sponge during a redox

process. It can change the pH near the surface of the electrode within a few tens ms and has high charge efficiency compared with other polymer based pH modulators.⁸ We conclude that it is possible to fabricate an electrically controllable proton sponge or pH modulator as a closed microcell. One example of applications of pH modulation is control of the reactivity of pH sensitive enzymes in the vicinity of the sulfonated polyaniline. For instance, we have taken 5 μl of chymotrypsin (5 mg ml^{-1} in 0.5 mol dm^{-3} NaCl) acting on 40 μl of succinyl-Ala-Ala-pro-phe-4-nitroanilide (5 mg ml^{-1} in 0.5 mol dm^{-3} NaCl) placed on the surface of a sulfonated polyaniline coated onto a Pt electrode. The ratio (R) of the absorbances at 375 nm (converted substrate) to 320 nm (unconverted substrate) varies with the oxidation states of sulfonated polyaniline. For example, for sulfonated polyaniline held at 0.30, 0.10 and -0.20 V vs. Ag for a 20 min reaction time, $R = 1.36$, 1.26 and 0.94, respectively, demonstrating electronic control of chemical reactivity of enzymes.

This research has been supported in part by the Defense

Advanced Research Projects Agency through a contract monitored by the US Office of Naval Research.

Received, 30th June 1992; Com. 2/03468I

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