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"PROTON TRANSPORT ON MODIFIED SULFONATED POLYANILINE ELECTRODE"

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February 18, 1991

Proton Transport on Modified Sulfonated Polyaniline Electrode

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ABSTRACT

The pH in the vicinity of a thin self-doped conducting polyaniline electrode was electrochemically modulated in aqueous solutions using both cyclic voltammetry and step potential techniques. Changes in pH were measured directly by using a microcombination pH probe. The experimental evidences verify the mechanism that the polymer behaves as a proton ejectors during oxidation and absorbers during reduction. This potential-controlled pH change near the polymer coated electrode may be applied to many fields such as an electric controller of the proton environment near the electrode surface.

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of the solution is decreased. After the reversal of the scan direction, the flow of cathodic current resulted in neutralization of polarons and subsequently absorbing protons, the pH changed 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 in half-wave potential.² The direct measurement of the pH change under the modulation of the potential supports the mechanism proposed previously.² 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 indicate that the pH change which accompanies the redox process tracks the charge consumption, and releasing and absorbing of protons were reversible.

Fig. 3 shows the pH change near the surface of the film electrode caused by the potential step between -0.1 and 0.35 V vs. Ag/AgCl(sat.). It can be seen again that the pH was decreased by the oxidation and increased by reduction of the polymer. The one to one corresponding relationship between potential and pH is found. The magnitude of pH change per volt is dependent on the pH of the electrolyte. For example, the pH change is 3.5 pH/Volt in pH ~ 3 solution while the change is 7.5 in pH ~ 6 electrolyte.

Due to the response time limit of the microcombination pH probe, the time profile of the pH change in a fast sweep is slower than the time profile of the doping charge of the sulfonated polyaniline film. However, it was found that sulfonated polyaniline exhibits a reversible p-type electrochemical dop-

ing with an association of high contrast color change and excellent stability.² Therefore, according to the mechanism proposed above, one can correlate the change in pH with optical change in a fast sweep experiment. In order to do this, we used a He-Ne laser beam which was reflected from the surface of the film and detected by a PIN photodiode. Following the application of a square voltage pulse, both the electrical response and the optical response were measured, see Fig. 4. The square wave response from the photodiode represents the changes in the reflected light intensity resulting from the switching reaction of the polymer, i.e. the changes in optical density correlated with changes in pH on the surface of the polymer. The characteristic response of optical density is about 10 ms. Generally, the charge transfer process consists of physical diffusion of redox species and self-electron transfer between the redox sites. Since conducting sulfonated polyaniline has relatively high charge mobility,² the diffusion time of proton in the polymer film is the dominant factor of the time response of the pH change in the vicinity of the electrode. This can be noted from that the current decays faster than the electrochromic response. The explanation of this is as the charge is brought to the surface of the film electrode rapidly and then diffuses into the bulk of the polymer more slowly.³ The later process is limited by the diffusion of protons in the polymer and is the rate controlling step.

Sulfonated polyaniline is durable at $\text{pH} \leq 4$ and potential lower than 0.35 V vs. Ag/AgCl. For example, the optical density remained more than 80% after 7 million cycles in 1 M HCl.

The experimental results demonstrate that sulfonated polyaniline be-

haved as a proton sponge during a redox process. It can change the pH near the surface of the electrode within few tens ms and has high charge efficiency compared to other polymer based pH modulator.⁴ We conclude that it is possible to fabricate an electrically controllable proton sponge or pH modulator in a closed micro-cell.

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- ³Yashima, Y.; Kobayashi, M.; Lee, K.B.; Chung, D.; Heeger, A.J.; Wudl, F. *J. Electrochem. Soc.* **1987**, *134*, 46-52.
- ⁴Sawai, T.; Shinohara, H.; Ikariyama, Y.; Aizawa, M. *J. Electroanal. Chem.* **1990**, *283*, 221-230.

I. Figure Captions And Figures

Figure 1. Typical cyclic voltammograms (50 mV/s) of first redox process of sulfonated polyaniline, where the W.E. was a polymer coated Pt foil, the C.E. was a Pt foil and the R.E. was Ag/AgCl in 1.0 M HCl (—) and pH=3 buffer solutions (- - - -).

Figure 2. (A) Cyclic voltammogram of sulfonated polyaniline on a Pt electrode in 1.0 M NaCl, pH=3 solution. Scan rate = 10 mV/s. (B) pH curve obtained simultaneously with (A).

Figure 3. pH change in the vicinity of sulfonated polyaniline coated Pt electrode upon double step potential between -0.1 and 0.35 V in 1.0 M NaCl, the charge was of 0.2 mC.

Figure 4. Plot of the electrical and optical responses of a 1 μm sulfonated polyaniline film on a 25 mm² Pt foil in pH = 1 1.0 M NaCl solution. Step potential was from -0.1 to 0.4 V.

Fig. 1

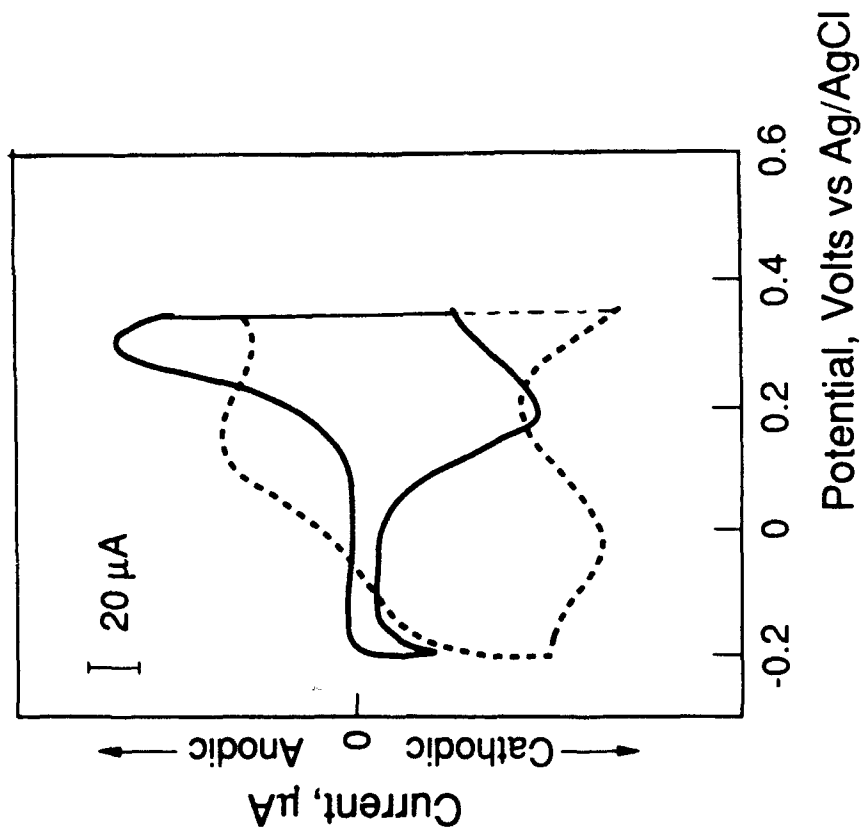
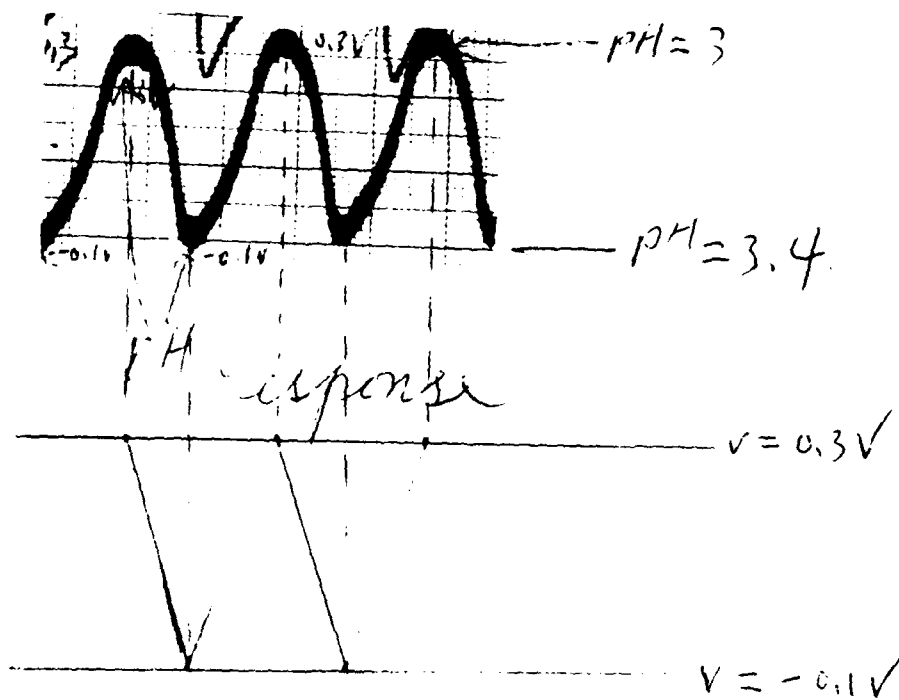
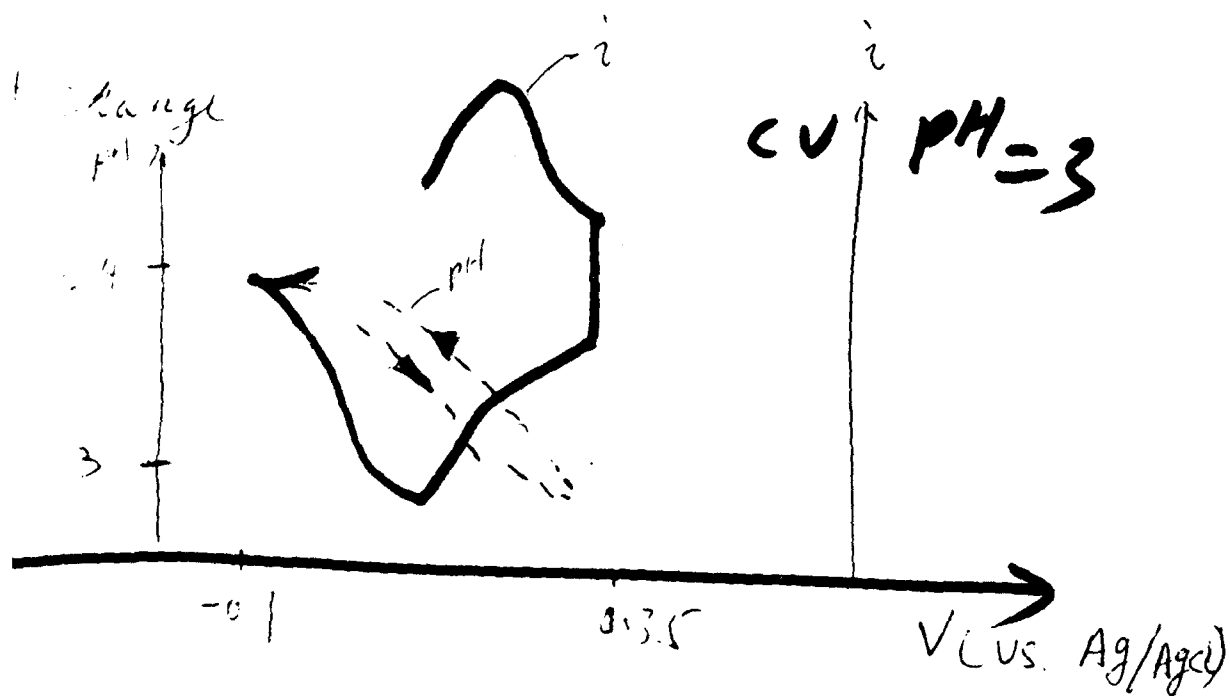
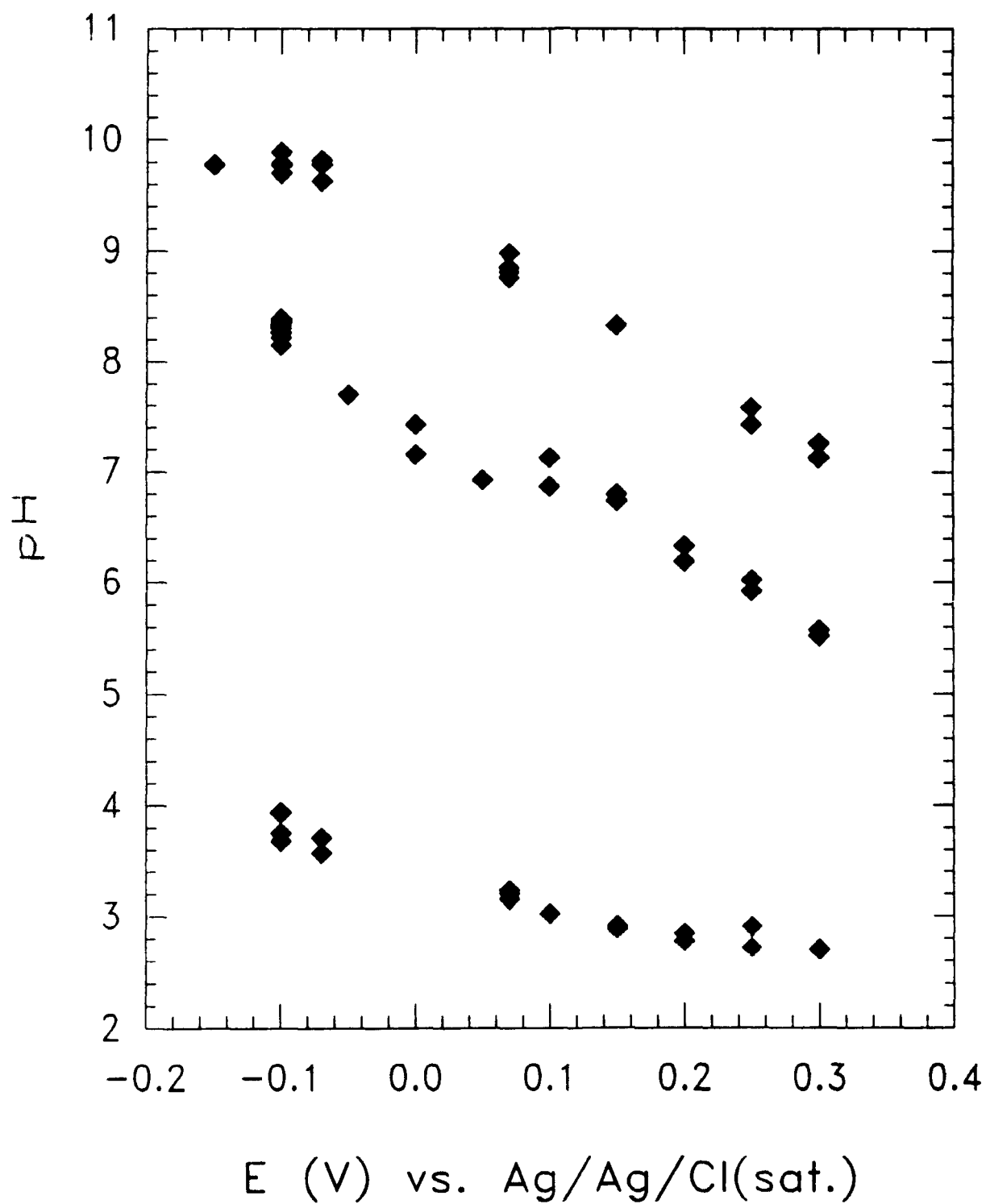


Fig 2.



pH modulation of SPAN



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