

pH-Dependent Mass and Volume Changes of Polypyrrole/Poly(styrene sulfonate)

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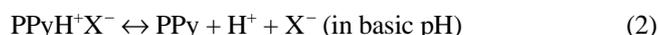
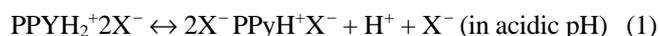
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It is well known that ion transport of polypyrrole (PPy) can be controlled by not only adjusting electric potentials,^{1,2} but also changing solution pH as in polyaniline.³ The former properties have been extensively studied for last a few decades, but the pH-induced ion transport of PPy might be more interesting for applications in some devices. For example, since ion movements of PPy result in the change of polymer volume,^{4,5} the control of ion transport by adjusting environmental pH can be utilized for the construction of pH-triggered drug-release-devices or microvalves⁶ with an aid of appropriate nanofabrication technologies.

The reason that pH-induced ion transport has received relatively less attention appears that PPy may experience deterioration in a basic solution due to OH⁻ attack on β -position of pyrrole rings, leading to irreversible degradation of π -conjugation of polymer backbone.⁷ Although π -conjugation is irreversibly broken in base, however, it seems more reasonable that the electrochemical property of PPy can be substantially recovered by subsequent acid treatments unless soaking time in a basic solution is too long.^{8,9}

For PPy doped with mobile anions, the effects of solution pH were reported by several authors using various methods.¹⁰⁻¹² Complex ion transport mechanisms were proposed especially in a basic solution (OH⁻ exchange vs. deprotonation of acidic proton of pyrrole units),¹²⁻¹⁵ but mass and volume changes of PPy doped with mobile anions were straightforward. Increase of solution pH leads to mass (volume) decreases, exhibiting two sudden transitions in acidic and basic pH ranges as follows.



In this paper, we first describe pH-induced ion transport behaviors of polypyrrole/poly(styrene sulfonate) (PPy/PSS) in various electrolytes using an Electrochemical Quartz Crystal Microbalance (EQCN), which have been expected to show simply opposite mass responses to PPy doped with mobile anions. This was performed since mass flow is a major factor to determine volume changes of PPy.^{4,5} We also present *in-situ* STM images demonstrating substantial volume changes of PPy/PSS with pH.

Experimental Section

Pyrrole (Aldrich) was passed over neutral alumina until

colorless before use. NaPSS, NaClO₄, KClO₄, CsClO₄, CsCl, CsOH (Aldrich), HClO₄ (Junsei, Japan), HCl (Daejung, Korea), NaOH, and KOH (Yakuri, Japan) were used as received.

PPy/PSS was synthesized on Au (geometric area = 0.21 cm²), evaporated on Ti/AT-cut quartz (9 MHz), in aq. solutions containing 0.1 M pyrrole and 0.1 M NaPSS at a fixed potential of +0.7 V until the desired charge was passed. The film thickness was calculated from the polymerization charge using a conversion factor of 2.5 $\mu\text{m C}^{-1} \text{cm}^2$.¹⁶ A Pt plate and a Ag wire were used as counter and reference electrodes. All the potentials cited in this paper were calibrated with respect to Ag/AgCl (3M KCl).

After preparation of PPy/PSS, films were redox-switched and maintained in 0.1 M electrolyte (pH = 6.8) solutions until the frequency change was negligible. Solution pH was adjusted by carefully adding a few tens μL of HClO₄ (or HCl) and NaOH (or KOH, CsOH) and the solution was gently mixed with a disposable pipette. It should be mentioned that frequency perturbation during mixing was not substantial, as compared with the pH-induced mass change. All the electrochemical and mass measurements were performed with a potentiostat and a quartz crystal analyzer (EQCN1000, NEWM Korea).

In order to investigate the volume change of PPy/PSS with pH, *in-situ* STM measurements (DI, Nanoscope E) were carried out. PPy/PSS was prepared on patterned Au plates. The procedure for patterning Au substrates with photoresist was described elsewhere in detail.⁴ Apiezon wax-coated Pt/Ir tips were utilized and images obtained in a constant current mode.

Results and Discussion

Figure 1 demonstrates mass changes of PPy/PSS (*ca.* 0.2 μm thick) in (A) NaClO₄, (B) KClO₄, and (C) CsClO₄ when solution pH was adjusted from 6.8 to (left) 11.9 and (right) 2.0 by adding HClO₄ and hydroxides of the same metal cations (NaOH, KOH, CsOH). On increasing pH from neutral pH, mass uptake occurs and the amounts of mass increase seem to be proportional to the cationic mass. This is not surprising since it is well known that PPy becomes insulating in a basic solution,⁸⁻¹² which requires influx of charge-balancing cations for PSS⁻. Note that no OH⁻ exchange mechanism can play a role in PPy/PSS unlike mobile anion-doped PPy,¹²⁻¹⁵ which makes mass responses reduced.

The change of solution pH to 2.0, however, results in

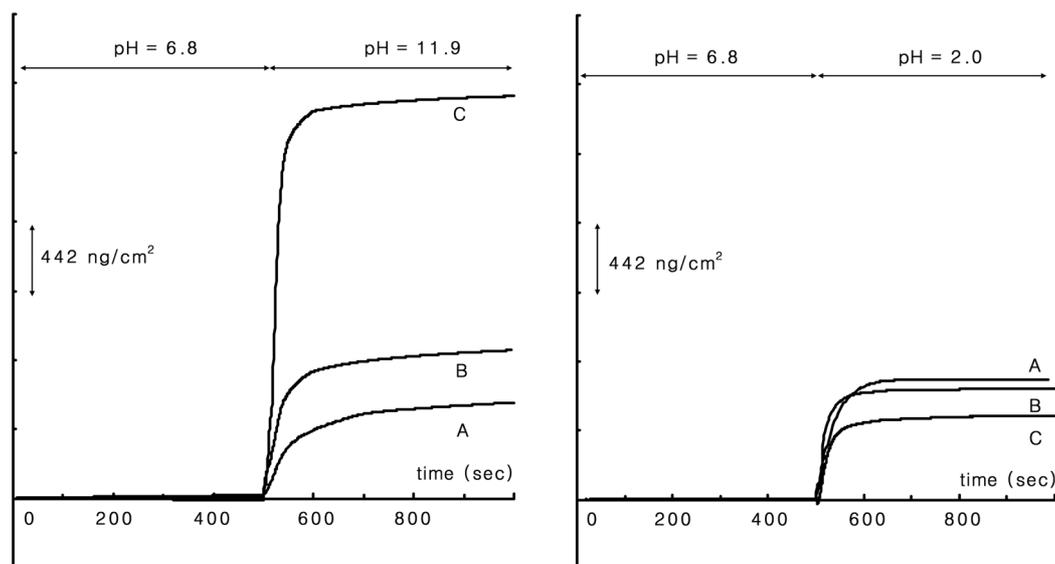
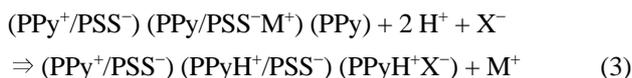


Figure 1. Mass changes of PPY/PSS (0.20 μm thick) in 0.1 M (A) NaClO_4 , (B) KClO_4 , and (C) CsClO_4 during changing solution pH from 6.8 to (left) 11.9 and (right) 2.0. pH was adjusted by adding HClO_4 and OH^- of the same counter cations.

rather complicated behaviors. Enrichment of H^+ in a medium leads to protonation of NH of pyrrole rings (pK_a of 2-4)¹⁰⁻¹² and incorporation of ClO_4^- into a PPY/PSS matrix. Considering a doping level of PPY/PSS at open circuit and ionic mass of ClO_4^- , mass increases after acid treatments should be greater than those shown in Figure 1 (right). In addition, the magnitudes of mass increases are also affected by cationic species. The greater the cationic mass, the smaller the mass increase. Therefore, Figure 1 (right) suggests that counter-flux of cations and anions occurs when solution pH is changed from neutral to acidic pH, due to the presence of PPY of different environments in neutral pH.



In order to further investigate mass responses of PPY/PSS (*ca.* 0.2 μm thick) with pH, solution pH was consecutively changed from neutral to acidic and basic pH. In addition to ClO_4^- electrolytes, CsCl was chosen to obtain the greatest mass changes in a wide pH range. As expected, Figure 2 shows that the smallest mass in neutral pH increases as pH is adjusted to acidic and basic pH in ClO_4^- and mass changes are significantly larger in a range of basic pH than acidic pH. This implies that PPY/PSS in ClO_4^- might be useful for the construction of a device such as an actuator requiring a small volume in neutral pH. In CsCl, mass responses continuously decrease down to $\text{pH} = \text{ca. } 4$ and stay stable below $\text{pH} = \text{ca. } 4$. These behaviors are likely to suggest that protonation of pyrrole units possessing $\text{PSS}^- \text{M}^+$ in vicinity favorably takes place in moderately acidic conditions (reaction 4) and free pyrrole units are predominantly protonated in highly acidic solutions (reaction 5), although counter flux is the case in a whole acidic pH range. It should be mentioned that no counter flux is in operation in basic pH as PPY/PSS in CsCl and CsClO_4 exhibits similar mass responses.

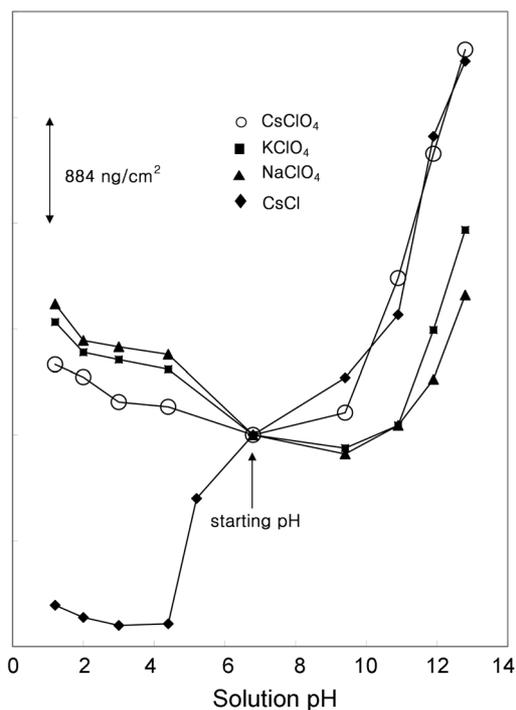
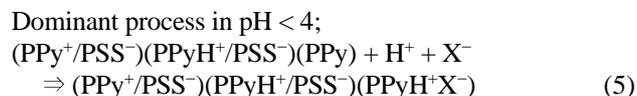
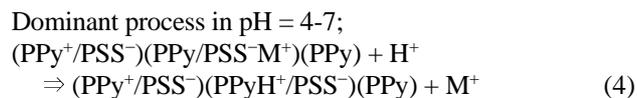


Figure 2. Mass changes of PPY/PSS (0.20 μm thick) during sequential control of solution pH. pH of CsCl was adjusted by adding HCl and CsOH.



It is also worth mentioning that these mass changes are reversible and independent of the starting pH. Although

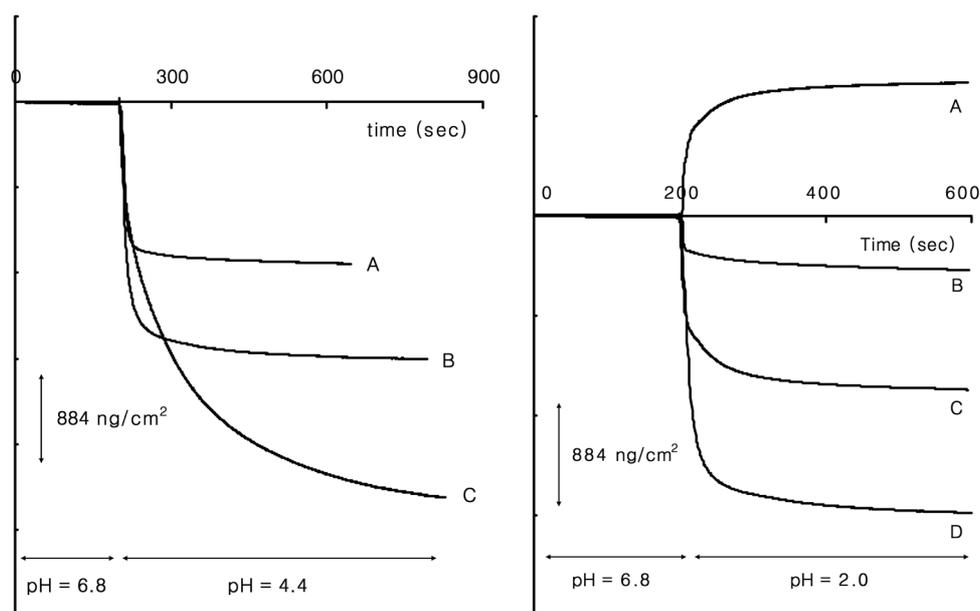


Figure 3. (left) Mass changes of PPy/PSS of (A) 0.20, (B) 0.4, and (C) 0.6 μm thick in CsCl during pH change from 6.8 to 4.4. (right) Mass changes of PPy/PSS (0.4 μm thick) in (A) 0.1 M CsClO₄, (B) 50 mM CsClO₄ and 50 mM CsCl, (C) 25 mM CsClO₄ and 75 mM CsCl, and (D) 0.1 M CsCl during pH change from 6.8 to 2.0. pH was adjusted with HCl and HClO₄ mixtures to maintain anionic compositions constant.

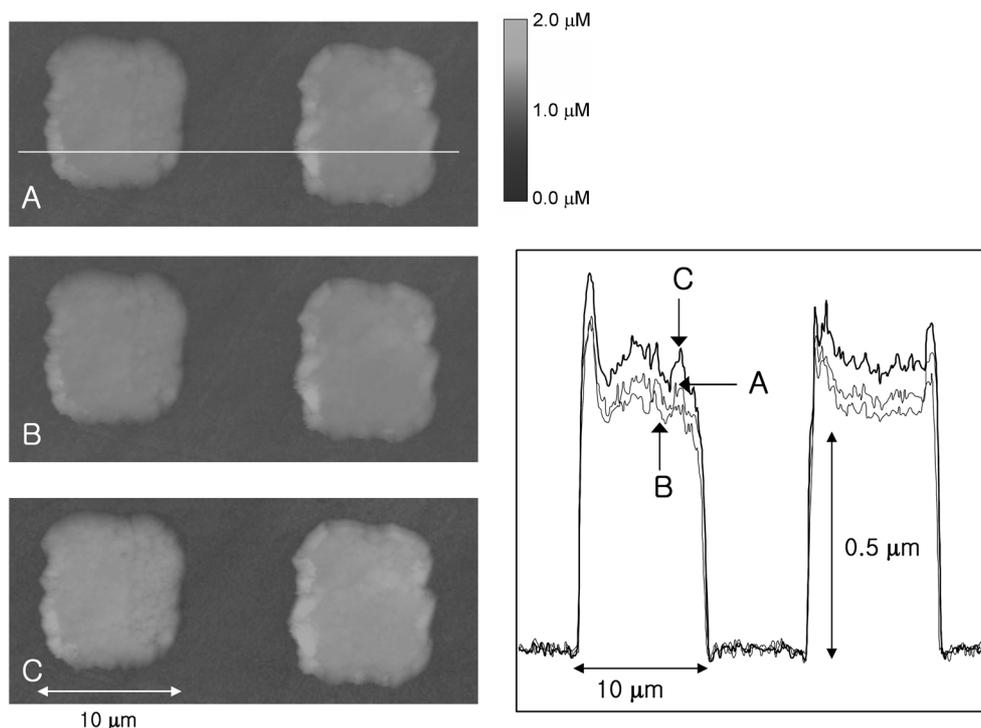


Figure 4. *In-situ* STM images and sectional profiles of PPy/PSS in CsCl of pH = (A) 6.8, (B) 3.0, and (C) 12.8.

Figure 2 shows the mass changes as pH is adjusted from 6.8, similar mass responses are resulted in as the starting pH is 12.8.

Figure 3 shows that the amount of mass (volume) changes can be easily controlled by adjusting film thicknesses or utilizing mixed electrolytes, which might be important for a device construction. Although a thick PPy/PSS needs longer equilibration time, Figure 3 (left) indicates that the magni-

tudes of mass changes are reasonably proportional to the film thickness. The film thicknesses of (A) 0.2, (B) 0.4, and (C) 0.6 μm produce the magnitudes of mass changes of (A) 1.6, (B) 2.6, and (C) 4.1 mg/cm^2 respectively. It should be noted, however, that the response time becomes longer as the increase of film thicknesses. This implies that optimal film thickness must be determined in consideration of response times as well as mass changes for a device construc-

tion. Figure 3 (right) also demonstrates the control of mass responses of PPy/PSS (0.4 μm thick) by changing electrolyte compositions. CsClO_4 and CsCl compositions were varied to be (A) 0.1 M : 0, (B) 50 mM : 50 mM, (C) 25 mM : 75 mM, and (D) 0 : 0.1 M. As explained previously in Figure 2, mass increases in 0.1 M CsClO_4 (A) and mass decreases in 0.1 M CsCl (D). In a mixed electrolytes, the presence of ClO_4^- affects more to the mass response over Cl^- since the mass decrease of (B) is 0.48 $\mu\text{g}/\text{cm}^2$ instead of 0.76 $\mu\text{g}/\text{cm}^2$ which is a medium value of (A) and (D).

Finally, to directly compare the mass with the volume change, *in-situ* STM was carried out for PP/PSS. Figure 4 shows $10 \times 10 \mu\text{m}^2$ PPy/PSS squares in CsCl of pH = (A) 6.8, (B) 3.0, and (C) 12.8. Sectional profiles indicate that the volume of PP/PSS is contracted by *ca.* 6% in pH = 3.0 and expanded by *ca.* 12% in pH = 12.8, relative to the one in pH = 6.8. The ratio of contraction *vs.* expansion is comparable to the mass responses shown in Figure 2. Relative to PP/PSS in CsCl of pH = 6.8, the mass decrease in pH = 3.0 is *ca.* 1.59 $\mu\text{g}/\text{cm}^2$ and the mass increase in pH = 12.8 *ca.* 3.12 $\mu\text{g}/\text{cm}^2$.

In conclusion, PPy/PSS exhibits cation-dependant mass increases with pH in a basic range, but rather complex mass responses in an acidic pH range. Both cation release and anion incorporation take place during reducing pH from a neutral. The latter appears dominant below pH = 4.0, making PPy/PSS in CsCl show the greatest mass and volume changes with pH.

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