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Cation Sensitivity of a Polypyrrole/Polyanion Composite Film Electrode

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Polypyrrole (PPy)/polyanion composite films were formed electrochemically in coexistence with a polymer electrolyte (poly(sodium 4-styrenesulfonate) (PSS) or poly(acrylic acid) (PAA)) in the polymerizing solution. The potential response behaviors of the PPy/PSS and PPy/PAA composites to cation activities were investigated, and the PPy/PSS electrode showed a better Nernstian response than that of the PPy/PAA electrode. The selection of incorporated polyanions and the polymerizing conditions, which were determined in this paper, affected the response behavior. The resultant PPy/PSS electrode showed a good Nernstian response only to monovalent cations with 58 mV/decade. The electrode indicated the equilibrium potential in a few seconds at the change of cation activity. It was found that the potential response was influenced by both the electroactivity of PPy and the PSS content in the PPy matrix.

Electropolymerization is one of an important method for the preparation of polymer-modified electrodes for various applications. Many reports on electropolymerization have been published, for fabrication of conducting polymer films,[1—3] some applications of electrochromic devices,[4,5] polymer batteries,[6,7] and functional electrodes.[8,9] In these cases, the key function of the electropolymerized film is electroactivity, which is produced by forming polarons, bipolarons, and solitons.[10]

Among various electropolymerized films, polypyrrole (PPy) films have a great advantage in their simplicity of synthesis. As-deposited PPy can be formed with a wide variety of electroactivities[11,12] and conductivities.[2,13—15] Previously, we reported that an insulating PPy thin film was applied to an amperometric pH sensor device for a very small test solution.[16]

Electropolymerized films are often utilized for the fabrication of functional electrodes having molecular selectivity, such as ion sensors,[17—20] gas sensors,[21—24] and biosensors.[25—28] In the case of a PPy film electrode doped with naphthalenesulfonate derivative anions, the electrode potential showed a Nernstian response to the activities of monovalent cations, and this response was influenced by the contents of the sulfonate group in the film.[29—31] The reason why the active PPy showed the Nernstian response, however, was not discussed clearly.

On the other hand, PPy films doped with polyanions can be formed electrochemically by the coexistence of the polyanions in the polymerizing solution as supporting electrolytes. During the formation of the PPy film, the anion species are fixed in the as-deposited polymer due to the compensation of the positive charge of PPy in situ, and the polyanions are incorporated into the PPy matrix.[32,33] An incorporated polyanion in the matrix can not be released due to its huge molecular volume and electrostatic interaction with the matrix. When the PPy is reduced electrochemically, the electroneutrality of the PPy/polyanion is conversed by penetration of the electrolyte cation, i.e., a reversible doping/undoping process of the cation. In our previous study, a composite PPy/polyanion film showed high electroactivity even in lithium battery cells.[34] In this research, we examine the cation potential response of PPy/polyanion composite films as basic properties to step up the PPy/polyanion composite films for micro cation sensors.

Experimental

Reagents. Reagent grade pyrrole (Wako Pure Chemicals Industries, Ltd.), poly(sodium 4-styrenesulfonate) (PSS) (Aldrich Chemical Co., MW ca. 70000) and poly(acrylic acid) (PAA) (Aldrich Chemical Co., average M.W. 250,000) were used without further purification. Tris-HCl buffer solution was used as a pH buffer. Deionized and distilled water was used throughout all the experiments.

Film Deposition by Electropolymerization. The PPy/PSS and PPy/PAA composite films were deposited on a Pt disk electrode (1 mmϕ) at a constant potential from aqueous solutions containing 0.25 mol dm^{-3} pyrrole monomer and either PSS or PAA as a supporting electrolyte. A one-compartment cell was assembled with Pt working, Pt auxiliary, and Ag/AgCl reference electrodes. The electrolyte solutions were deoxygenated by bubbling with nitrogen for 15 min prior to all electrochemical polymerizations and measurements. The working electrode was an epoxy resin-buried Pt disk polished to a mirror finish with 0.3 μm Al_2O_3 powder.

Potential Measurements of Film Electrode. After the deposition of the composite, the electrode was conditioned for two hours in a 1 mol dm^{-3} NaCl aqueous solution. The potentials of the film electrodes were measured in test solutions containing chloride salts of alkaline metals, alkaline earth metals and ammonium with a configuration cell of: Ag/AgCl, KCl(sat.) || *test solution* | composite polymer on Pt surface. The ionic activities of the test solutions were controlled by dropping aqueous solutions of various concentrations at room temperature and the liquid junction potential in the cell was not corrected. The pH-buffered solutions were prepared from 0.01 mol dm^{-3} Tris aqueous solutions and the pH value was adjusted using 0.1 mol dm^{-3} HCl.

Results and Discussion

Response Behavior of PPy/PSS and PPy/PAA. The PPy/PSS and PPy/PAA composite film electrodes were formed in aqueous pyrrole solutions containing PSS and PAA, respectively. Shimidzu et al. reported that both PPy/PSS and PPy/poly(vinyl sulfate) films showed good adhesion to the substrate and a mechanical intensity better than that of PPy doped with small anions.[35] The PPy/PSS and PPy/PAA films used in this study were also confirmed to be uniform black films showing good adhesion.

For the three electrodes, the electrode potentials were influenced by the change in the ionic activities in NaCl or $CaCl_2$ aqueous solutions, as shown in Fig. 1. The PPy/PSS and PPy/PAA composite films were formed under the same conditions from aqueous solutions containing 1 mol dm^{-3} PSS and PAA, respectively. In Fig. 1 a), bare Pt shows an unstable potential response to chloride anion with a negative slope. It seems that the response is due to the adsorption of chloride ion on the Pt surface. On the contrary, the electrodes modified with the composite films show Nernstian responses only to Na^+ with positive slopes and the response potential becomes stable in a few seconds after a change in the cation activity. This stability of the response potential is considered to be due to the high electroactivity of polypyrrole. These results indicate that the responses to Na^+ are due not to the Pt surface, but to the composite films over the Pt surface. Compared with the responses of the PPy/PAA electrode, the PPy/PSS electrode responded only to Na^+ with a larger slope and a lower response limit of -4.7 of log a. In the evaluation of the two films, the electroactivity of the electrode was examined by cyclic voltammetry.

Figure 2 shows cyclic voltammograms of the PPy/PSS and PPy/PAA electrodes. Evidently, the PPy/PSS electrode has a higher activity than that of the PPy/PAA electrode in the doping/undoping process of the cation. From previous investigations including our results, we believe that nucleophilic reagents attack the positive site of active PPy causing an irreversible structural change in the polypyrrole molecule, and PPy is made inactive.[15,36—39] As the carboxyl group of PAA is a stronger nucleophile than the sulfonate group of PSS, the PPy molecule may be somewhat decomposed in the PPy/PAA composite. As a result, the PPy/PSS electrode showed a higher activity and better response to Na^+ than that of the PPy/PAA electrode. Hence we chose the PPy/PSS composite for the following investigation of both the optimum conditions of deposition and the mechanism in regard to cation response.

Optimization of PPy/PSS Formation Conditions for Cation Response. The polymerizing conditions of the PPy/PSS influenced the response behavior. For the determination of the optimum preparation conditions of the PPy/PSS electrode, we investigated the influences of the amount of the film formation charge, the concentration of PSS in the polymerizing solution, and the polymerizing potential.

First, the dependence of the amount of the passing charge on the cation responses in shown in Fig. 3. From a cross-sectional observation using SEM, 0.05, 0.1, and 1 C cm^{-2} PPy/PSS films were uniform, dense and flat films of ca. 0.2, 0.4, and 4 μm thick, respectively. In the case of comparatively thin films (Fig. 3a) and b)), the PPy/PSS electrodes did not show a good response to the cation. A better Nernstian response to Na^+ was observed for the 1 C cm^{-2} electrode, as shown in Fig. 3c). These three composites were confirmed to have similar redox reaction doping rates in the cyclic voltammetry results. At more than 1 C cm^{-2} of passing charge, the PPy/PSS electrodes showed similar responses to that of the 1 C cm^{-2} electrode.

In increasing the amount of the passing charge up to 1 C cm^{-2}, the onset potentials of these electrodes shifted down from 300 mV for 0.05 C cm^{-2} to -50 mV for 1 C cm^{-2}, while in Fig. 1a) the bare Pt electrode indicated a potential around 400 mV. In consideration of these results, it is believed that the thin PPy/PSS electrode shows a mixed potential of both the composite and the Pt surface because of permeation of the test solution through the thin PPy/PSS film. The thick PPy/PSS film at more than 1 C cm^{-2} could probably protect the Pt surface from this permeation. The free-standing PPy/PSS film electrode, which is peeled from a Pt substrate, is expected to show a Nernstian response to Na^+ ion independent of the amount of the passing charges. For a good Nernstian responses to cations of the Pt electrode coated with the PPy/PSS film, the amount of formation charge more than 1 C cm^{-2} was sufficient for the response.

In the Ca^{2+} activity range over 10^{-3}, the electrode potentials decreased dramatically (Fig. 3) and the re-

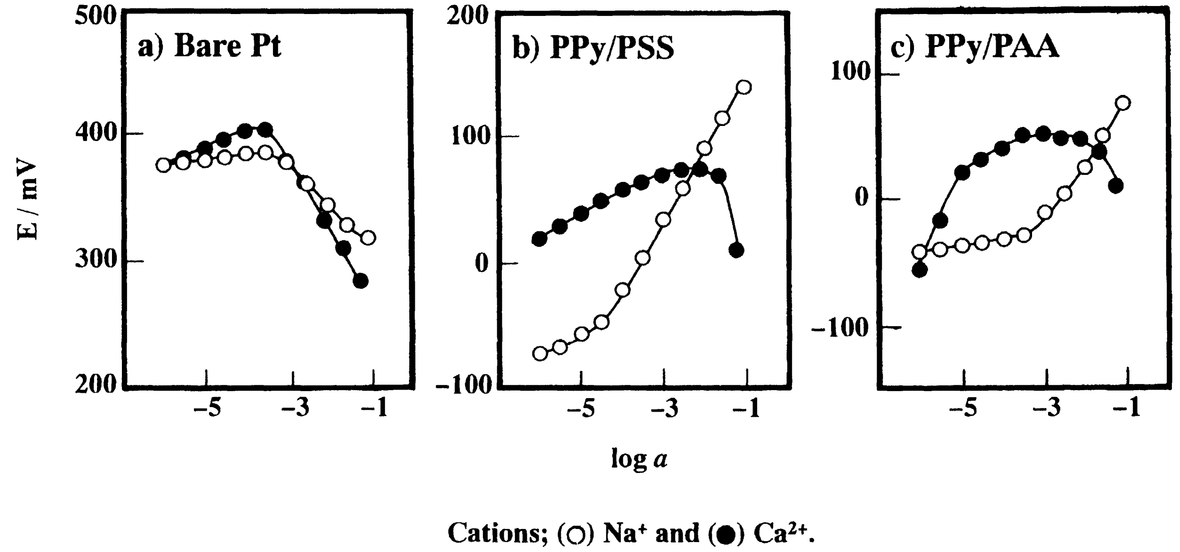

Fig. 1. Potential response of a) a bare Pt electrode, b) PPy/PSS, and c) PPy/PAA composite film electrodes. PPy/polyanion films were formed on Pt from 0.25 mol dm^{-3} pyrrole and 1 mol dm^{-3} polymer electrolyte aqueous solutions at 0.8 V vs. Ag/AgCl with 1 C cm^{-2}. Log *a* is the logarithm of the activity of cations.

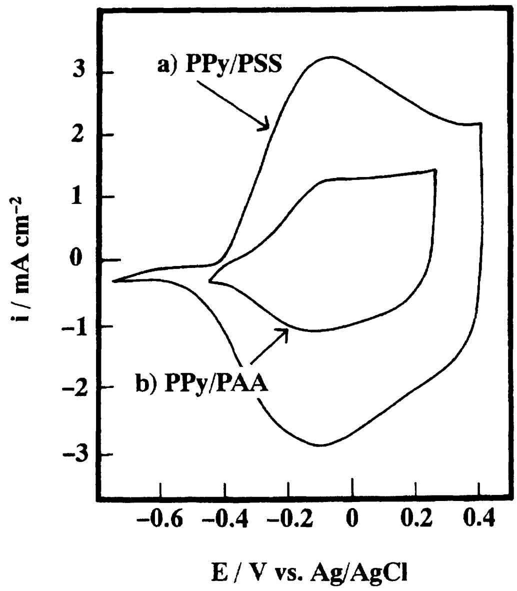

Fig. 2. Cyclic voltammograms of a) PPy/PSS and b) PPy/PAA composite film electrodes in a 1 mol dm^{-3} $LiClO_4$ aqueous solution at 20 mV s^{-1}. PPy/polyanion films were formed on Pt from 0.25 mol dm^{-3} pyrrole and 0.2 mol dm^{-3} polymer electrolyte aqueous solutions at 0.75 V vs. Ag/AgCl with 1 C cm^{-2}.

lationship showed nonlinearity. This suggests that two sulfonate groups and a calcium ion form ion pairing precipitation in the film in this region, and this composite film can switch from a cation exchange to an anion exchange membrane. This reaction is reversible with rinsing in water. We confirmed that after dropping $CaCl_2$ solution into a poly(sodium 4-styrenesulfonate) aqueous solution, a white gypsum-like precipitate appeared.

Next, the dependence of the PSS concentration in aqueous pyrrole solutions on the cation responses was investigated. Figure 4 shows the PPy/PSS electrode potential responses, which were formed from solutions of 0.01, 0.2, and 1 mol dm^{-3} PSS anionic group with 1 C cm^{-2} of passing charge. Using very low concentration (0.01 mol dm^{-3}) PSS, the electrode indicated an unstable potential in the low concentration region between −6 and −5 of log *a* and responded to chloride anion with negative slopes in the log *a* region greater than −4. These responses were similar to those of the PPy-modified electrodes doped with chloride anion.[28] On the other hand, the PPy/PSS electrodes prepared from 0.2 and 1 mol dm^{-3} PSS show Nernstian responses to Na^+. The response potential of 1 mol dm^{-3} PSS was more stable and had a slightly larger slope than that of 0.2 mol dm^{-3} PSS. When the PPy/PSS film was formed from a 1.5 mol dm^{-3} PSS solution, which was an almost saturated solution and had a high viscosity, the PPy/PSS electrode showed a response similar to Fig. 4c). The optimum concentration of poly(sodium 4-styrenesulfonate), therefore, was more than 1 mol dm^{-3}.

The increase in PSS concentration was accompanied by a down-shift of the onset response potential, from 300 mV for 0.01 mol dm^{-3} to −50 mV for 1 mol dm^{-3} as shown in Fig. 4. This suggests that the negative part of the sulfonate group, which doesn't form an ion pair with both the cation and the positive PPy site, increases with the addition of PSS in a polymerizing solution and the content of the sulfonate group also increases. The negative group on PSS and the high content of PSS in the composite perhaps have advantages leading to a good cation response. In consideration of this explanation, it is reasonable that the good response to Na^+ is

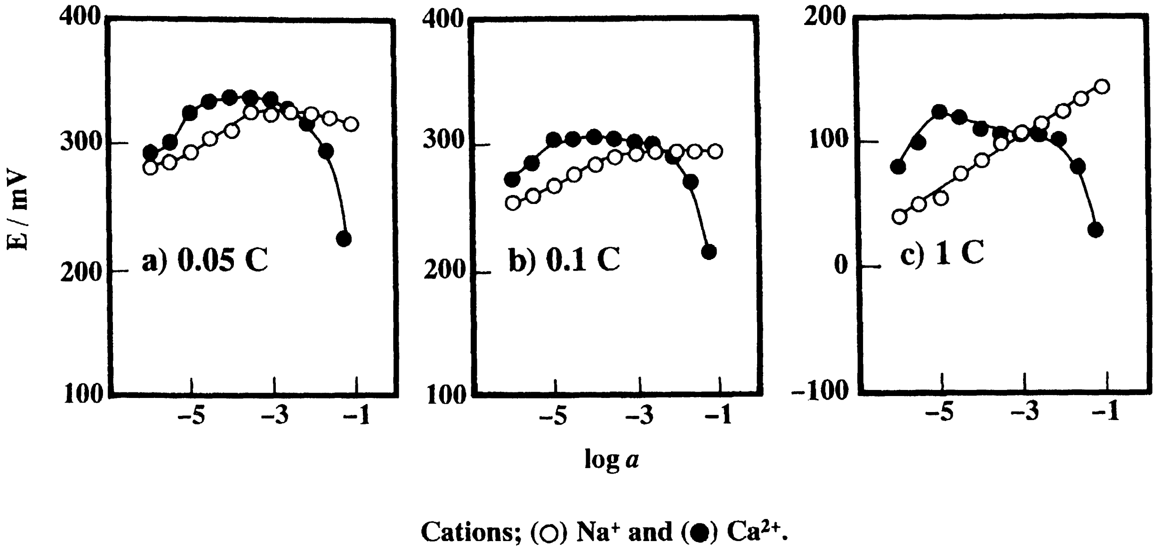

Fig. 3. Potential responses of PPy/PSS composite film electrodes formed on Pt from a 0.25 mol dm^{-3} pyrrole and 0.2 mol dm^{-3} PSS aqueous solution at 0.8 V vs. Ag/AgCl with a) 0.05, b) 0.1, and c) 1 C cm^{-2}. Log *a* is the logarithm of the activity of cations.

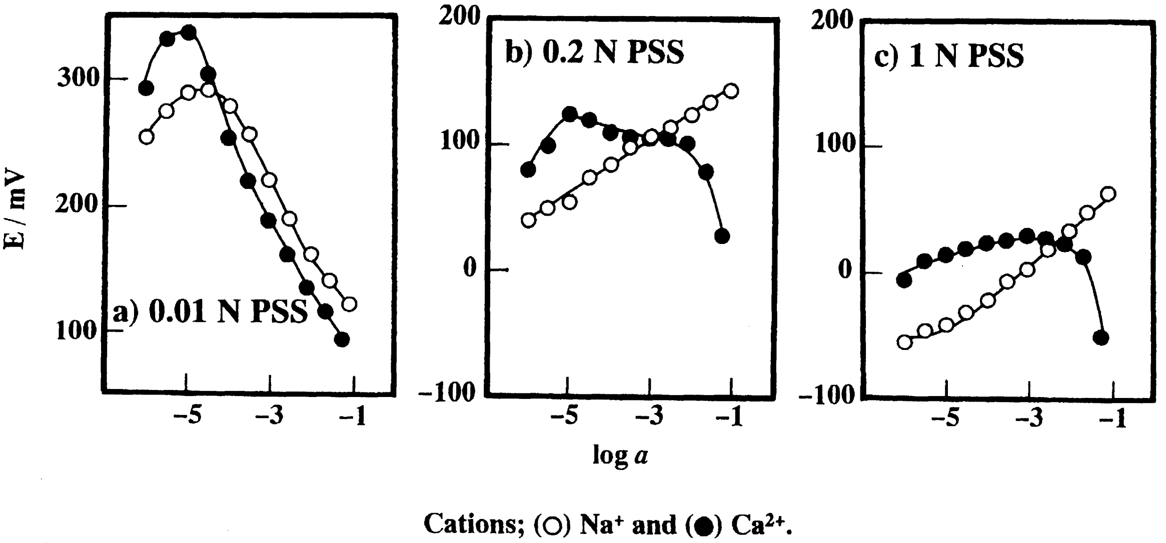

Fig. 4. Potential responses of PPy/PSS composite film electrodes formed on Pt from a 0.25 mol dm^{-3} pyrrole and a) 0.01, b) 0.2, and c) 1 mol dm^{-3} PSS aqueous solutions at 0.55 V vs. Ag/AgCl with 1 C cm^{-2}. Log *a* is the logarithm of the activity of cations.

accompanied by the down-shift of the response potential as is shown in Fig. 4.

Figure 5 shows the responses of the PPy/PSS electrodes formed at different potentials to various cations. When the PPy/PSS film was formed at 0.55 V, the electrode responded to activities of alkaline metal ions with a slope of 32 mV/decade as indicated in Fig. 5a). At formation potentials of 1.1 and 1.5 V, although these electrodes show better responses only to alkaline metal ions with larger slopes in Fig. 5c) and d), the response indicates low reproducibility in successive measurements. The PPy/PSS electrode formed at 0.8 V shows a stable and more reproducible response with a slope of 58 mV/decade as shown in Fig. 5b).

The cyclic voltammograms of these PPy/PSS electrodes are shown in Fig. 6. Degradation of activity of the PPy/PSS electrode appears when the formation potential is on the positive side. The potential difference between the anodic and cathodic peaks becomes larger with an increase in the formation potential, which may be due to a lower electrochemical reversibility and/or lower conductivity of the PPy/PSS electrode with increasing formation potential. This is considered to be due to overoxidation of the PPy molecule as already discussed.[15] The activity of the PPy/PSS electrode approximately increased with decreasing the deposition potential and doping rates were 23.3, 18.2, 14.9, and 17.0% for polymerizing potentials of 0.55, 0.8, 1.1, and

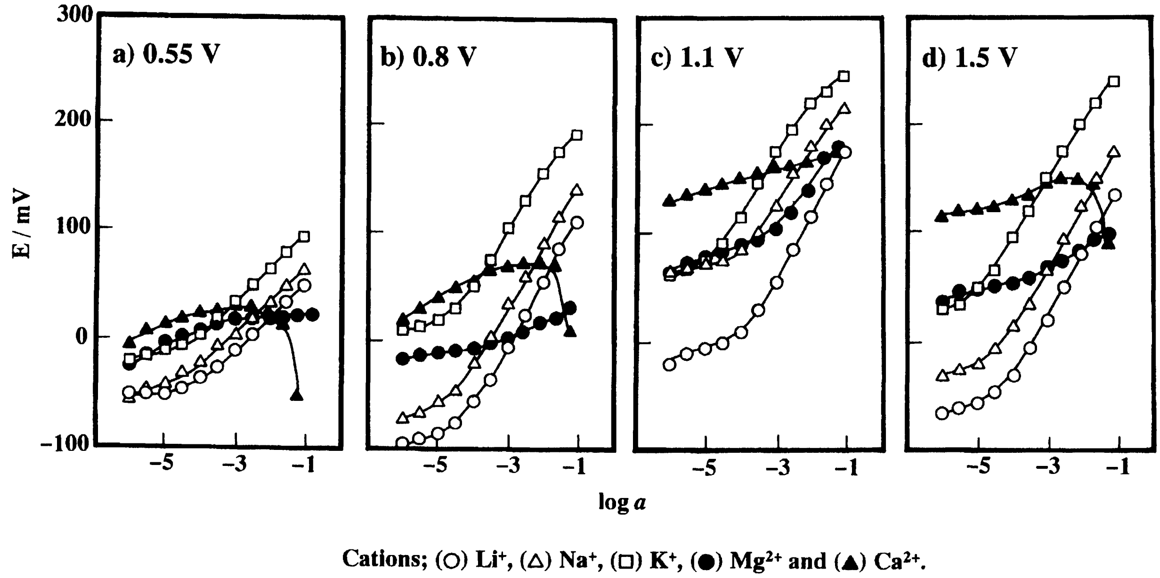

Fig. 5. Potential responses of PPy/PSS composite film electrodes formed on Pt from a 0.25 mol dm^{-3} pyrrole and 1 mol dm^{-3} PSS aqueous solution at a) 0.55, b) 0.8, c) 1.1, and d) 1.5 V vs. Ag/AgCl with 1 C cm^{-2}. Log a is the logarithm of the activity of cations.

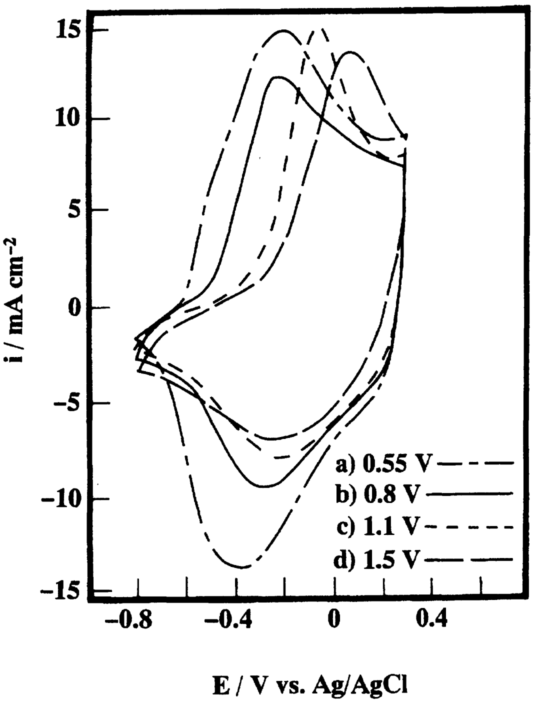

Fig. 6. Cyclic voltammograms of PPy/PSS composite film electrodes in a 0.5 mol dm^{-3} PSS aqueous solution at 100 mV s^{-1}. PPy/PSS films were formed on Pt from 0.25 mol dm^{-3} pyrrole and 1.0 mol dm^{-3} PSS aqueous solution at a) 0.55, b) 0.8, c) 1.1, and d) 1.5 V vs. Ag/AgCl with 1 C cm^{-2}.

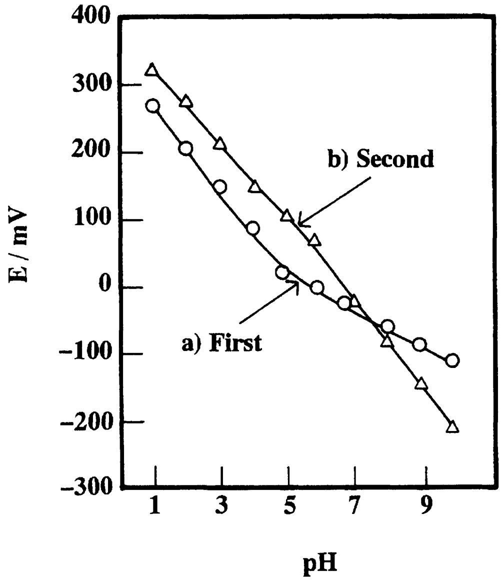

Fig. 7. Potential responses of a PPy/PSS composite film electrode with change in pH formed on Pt from a 0.25 mol dm^{-3} pyrrole and 1 mol dm^{-3} PSS aqueous solution at 0.8 V vs. Ag/AgCl with 1 C cm^{-2} in a) the first and b) the second measurements.

1.5 V, respectively. On the other hand, the sulfonate group content in the composite slightly increased with higher electrode potential, probably due to the electrophoresis of the negatively charged-PSS molecule. It may be that there are two factors affecting the response to cations which are contrary to each other against the formation potential, i.e., the electroactivity of PPy and the PSS content in the matrix. It seemed that the optimum formation potential of 0.8 V was determined by a compromise of these two factors.

The shift-up of the response potential range appeared in repeating measurements in Fig. 5. We considered that this shift of the response was caused by the change in the pH value of the test solution because it was not buffered. Since the pH response of the active PPy film

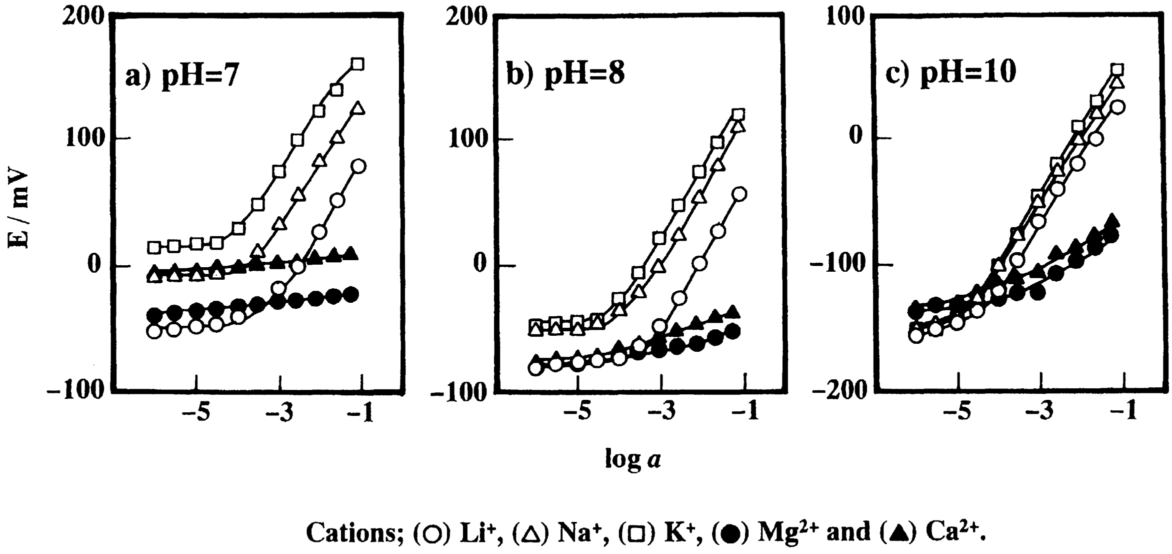

Fig. 8. Potential responses of PPy/PSS composite film electrodes formed on Pt from a 0.25 mol dm^{-3} pyrrole and 1 mol dm^{-3} PSS aqueous solution at 0.8 V vs. Ag/AgCl with 1 C cm^{-2} in pH buffered solution of a) pH=7, b) pH=8, and c) pH=10. Log a is the logarithm of the activity of cations.

was reported,[18] the pH value in the test solution was adjusted as described in the next section.

Dependence on the pH Value of the Test Solution. Figure 7 shows a potential–pH diagram of the optimized PPy/PSS film electrode. The pH values were controlled from 9.9 to 1.0 by dropping 0.1 mol dm^{-3} HCl aqueous solution into 0.01 mol dm^{-3} Tris buffer solution. The concentration of Tris between 0.001 and 0.03 mol dm^{-3} was almost independent of the electrode potential of the PPy/PSS electrode. A Nernstian relationship appeared in the diagram, but the response potentials were different between the first and second measurements due to the slow protonation rate of active PPy.[18] The subsequent response curves after the second measurement, however, nearly overlapped each other.

Next we investigated the response of the optimized PPy/PSS electrode in pH buffered solutions, as shown in Fig. 8. In Fig. 8c), for a high pH value, the PPy/PSS electrode showed good responses to Li^+, Na^+, and K^+ in the log a region greater than −5, although it somewhat responded to Ca^{2+} and Mg^{2+} ions with a slope around 19 mV/decade. Decreasing the pH value, as shown in Fig. 8a) and b), made the slope of the response to alkaline earth metal ions smaller. Thus, in the pH=7 test solution the PPy/PSS electrode shows a selective response only to alkaline metal ions and shows almost no response to Mg^{2+} and Ca^{2+}. The PPy/PSS electrode also responded to ammonium ion in a manner similar to alkaline metal ions. The PPy/PSS electrode was thus confirmed to respond only to monovalent cations. The selective response only to K^+ will be achieved by a formation of a plasticized poly(vinyl chloride) membrane onto the PPy/PSS electrode.[40)]

Influence of Overoxidation of PPy/PSS. We previously reported that the application of an anomalously positive potential sometimes decreased the original conductivity and electroactivity of PPy, i.e., the occurrence of irreversible oxidation ("overoxidation").[15] The influence of overoxidation on the response of the PPy/PSS electrode may make clear the response mechanism. When overoxidation was applied to the PPy/PSS composite film electrode, which has never been reported, the PPy/PSS electrode was unresponsive to cations as is shown later.

After application of a potential of more than 1.0 V in an aqueous solution, the composite film showed weakened adhesion to the Pt surface and less electroactivity. Thus, we carried out the inactivation treatment of the PPy/PSS electrode by 10 cycles of potential scanning up to 0.9 V. This treatment inactivated the PPy/PSS electrode as is shown in Fig. 9. From the EPMA spectra of both the as-prepared and inactivated PPy/PSS film, the contents of sulfur were almost same. This suggests that anodic insertion of cations is caused instead of anodic release of anions,[37] and the PSS molecule remains in the matrix after the carbonyl group is formed by overoxidation.[36] As a result, the redox site in the PPy/PSS film decreases.

Figure 10 shows the potential response to cations to the inactivated PPy/PSS electrode. This is different from that of the as-prepared PPy/PSS electrode, and the inactivated composite film electrode showed no Nernstian response. From this, although the content of the sulfonate group is high in the composite, inactivation of the PPy molecule interferes with the response to cations.

In addition to its electrochemically active nature, the composite film showed the ability to exchange cations between the adjacent solution and the composite film.

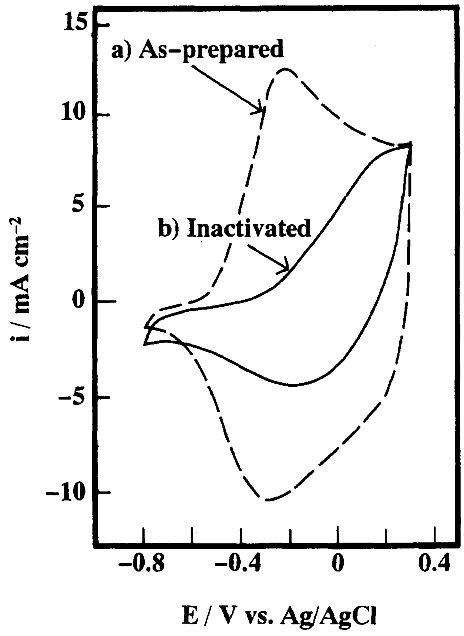

Fig. 9. Cyclic voltammograms of a) as-prepared PPy/PSS and b) inactivated PPy/PSS composite film electrodes in a 0.5 mol dm^{-3} PSS aqueous solution at 100 mV s^{-1}. PPy/PSS composite films were formed on Pt from a 0.25 mol dm^{-3} pyrrole and 1 mol dm^{-3} PSS aqueous solution at 0.8 V vs. Ag/AgCl with 1 C cm^{-2}, and an inactivation treatment of a PPy/PSS film was carried out by 10 cycles of potential scan between −0.8 V and 0.9 V vs. Ag/AgCl in the same condition.

Because the PPy/PSS electrode has a redox potential, the Nernst equation can be applicable to these potential responses:

$$\mathrm{PPy^{+}PSS^{-}+M^{+}+e^{-}} \rightleftarrows \mathrm{PPy^{0}+PSS^{-}M^{+}}$$
$$E=\mathrm{const.}+RT/F\ln\{([\mathrm{PPy^{+}PSS^{-}}][\mathrm{M^{+}}])/([\mathrm{PPy^{0}}][\mathrm{PSS^{-}M^{+}}])\}, \tag{1}$$

where $[\mathrm{PPy^{+}PSS^{-}}]$, $[\mathrm{PSS^{-}M^{+}}]$, $[\mathrm{PPy^{0}}]$, and $[\mathrm{M^{+}}]$ are the concentrations of an ion couple of a charged PPy and a PSS sulfonate group, the cation sulfonate salt in the film, neutral PPy which can work as an active site, and the cation of the test solution, respectively. For the system under investigation here, these factors became constant values except for $[\mathrm{M^{+}}]$ in this equation. So, Eq. 1 was simplified as follows:

$$\begin{aligned} E &= \mathrm{const.}+RT/F\ln[\mathrm{M^{+}}] \\ &= \mathrm{const.}+0.059\log[\mathrm{M^{+}}] \quad \text{at } 25\,^{\circ}\mathrm{C}. \end{aligned} \tag{2}$$

"E" is the potential of the composite electrode which is able to respond to the logarithm of the monovalent cation activities as is shown in Fig. 8. In the case of the inactivated polypyrrole, it has no redox site and thus Eq. 2 is not applicable to the system, where the PPy/PSS electrode indicates no response as is shown in Fig. 10.

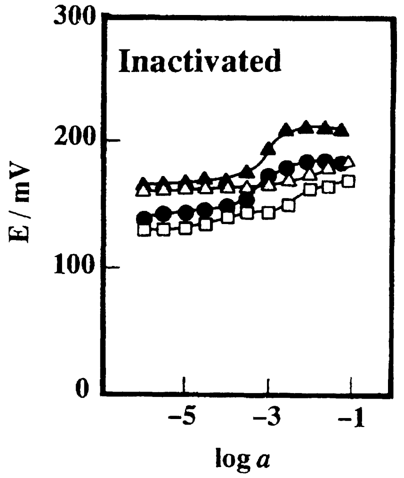

Fig. 10. Potential responses of an inactivated PPy/PSS composite film electrode formed on Pt from a 0.25 mol dm^{-3} pyrrole and 1 mol dm^{-3} PSS aqueous solution at 0.8 V vs. Ag/AgCl with 1 C cm^{-2}, and an inactivation treatment of a PPy/PSS film was carried out by 10 cycles of potential scan between −0.8 V and 0.9 V vs. Ag/AgCl in a 0.5 mol dm^{-3} PSS aqueous solution at 100 mV s^{-1}. Log *a* is the logarithm of the activity of cations.

As is shown in Fig. 8, the response to divalent cations seems to be able to adopt the Nernstian equation. In the case of the pH=10 test solution, the steep slope of 19 mV is interpreted by 3 electrons per one divalent cation as in the following equation:

$$\begin{aligned} &\mathrm{3PPy^{+}PSS^{-}+M^{2+}+H^{+}+3e^{-}} \\ &\quad \rightleftarrows \mathrm{3PPy^{0}+2PSS^{-}M^{2+}+PSS^{-}H^{+}} \end{aligned}$$

and in the pH=10 buffered solution,

$$E=\mathrm{const.}+0.020\log[\mathrm{M^{2+}}] \quad \text{at } 25\,^{\circ}\mathrm{C}. \tag{3}$$

The equation can probably be adopted in this case. By decreasing the pH value, the PPy/PSS electrode might respond to divalent cations with a gentler slope due to the effect of the protons as shown in Fig. 8.

From only these dynamic experiments, however, there is no evidence related to the origin of the selective response to monovalent cations versus divalent cations. The selectivity of the composite may possibly be attributed to the mobility of cations at the composite/solution interface.[41) This mobility could be affected by ion pairing and the ionic radii. It also seems that the selectivity may be due to the difference of ability in the charge compensation of each cation in the composite film.

Conclusions

PPy/PSS and PPy/PAA composite films were formed electrochemically in the coexistence of a polymer electrolyte. The PPy/PSS electrode showed a better Nernstian response than the PPy/PAA electrode. The optimum conditions for the preparation of the PPy/PSS film were determined and the optimum PPy/PSS electrode showed the Nernstian response well only to alkaline metal and ammonium ions. It was found that the potential response was effected by both the electroactivity of PPy and the PSS content in the PPy matrix. It may be possible to fabricate molecular functional electrodes based on the composite after further study.

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