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Hydronium Ion Response of Some Polypyrrole Coated Metallic Electrodes

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Polypyrrole (PPy) has received a great attention because of its good electrical conductivity. Most of the studies on polypyrrole as an organic conducting polymer have been focused on understanding the structure and properties of PPy film and on enhancing the stability of photoelectrodes used in converting solar energy to electrical or chemical energy.[1~8] However, only a few applications have employed PPy modified electrodes as ion-sensing electrodes.[9~14] Although the PPy modified electrode is not considered to be an ion-selective electrode,[11] it appears to be possible to make the electrode to be selective to an anion by changing the conditions used in the electropolymerization. Recently, it has been demonstrated that the PPy film on Pt shows a stable and selective potential response towards H_3O^+ ions in solution.[10] It is the aim of this paper to extend the investigation to other metals, such as stainless steel, Cr, Nb, Ta, and zircaloy. It is reported here that the preparation and electrical responses of the PPy modified metal electrodes for the purpose of utilizing them as potentiometric sensors for hydronium ion.

Experimental

All chemicals, if not otherwise mentioned, were reagent grade and used without further purification. Pyrrole (Fluka AF, purum) was vacuum distilled with NaH and stored in refrigerator. All solutions were deoxygenated with a stream of 99.99% Ar gas within an electrochemical cell before measurement. The pH of solution was adjusted with H_3PO_4/KH_2PO_4, KH_2PO_4/K_2HPO_4, and K_2HPO_4/K_3PO_4 buffer solutions. All the electrode materials were of 99.9% purity. Zircaloy was obtained from the cladding material for nuclear fuel.

A polypyrrole (PPy) coated electrode was prepared on a polished metal electrode from an aqueous solution containing 50 mM pyrrole and 1.0 M HNO_3 using cyclic voltammetry as described previously.[8] Polishing the metal was performed using Al_2O_3 powder. Polymer film was coated by scanning 10 times over the range from −0.20 V to 0.5 V above the initiation voltage (see below) at the scan rate of 100 mV/sec. All potentials are reported against a Ag/AgCl electrode at 25 °C.

The electrochemical measurement was carried out with a PPy coated metal working electrode, a platinum coil counter electrode separated by a Vycor frit, and a Ag/AgCl reference electrode connected to the analyzing compartment th-rough a Vycor frit. A Princeton Applied Research Model 273 potentiostat/galvanostat and RE0091 X-Y recorder were used for electrochemical polymerization. All potential responses were measured with a Horiba Model F-7 ssII pH meter.

Results and Discussion

To obtain the potential for the polymerization, cyclic voltammetry was used. Figure 1 shows the first cyclic voltammograms of 50 mM pyrrole in 1.0 M HNO_3 with stainless steel (SS306), Cr, and Nb electrodes at a scan rate of 100 mV/sec. The anodic current leading to broad peaks at about 1.0 V initiates apparently to flow near 0.74 V, 0.75 V, and 0.84 V for stainless steel, Cr, and Nb, respectively, and beyond the broad maximum passivations occur. For Pt, Ta, and zircaloy the initiation voltages were similarly found to be 0.74 V, 0.81 V, and 0.85 V, respectively. However Fe, Cu, and Al could not be electrocoated with polypyrrole in agreement with the results previously reported.[15] Fe and Cu were anodically dissolved and oxide growth dominated over the electropolymerization for Al.

When the direction of scan was reversed before the broad maximum but larger than the initiation voltage, the current increased progressively with the number of cycles. The broad
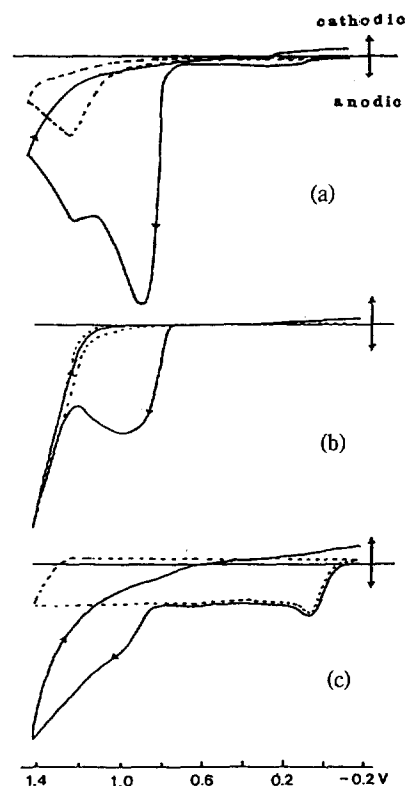

Figure 1. The first cyclic voltammograms of metal electrodes in aqueous 1.0 M HNO_3 containing 50 mM pyrrole. Metal: (a) stainless steel, (b) Cr, (c) Nb. Dotted curve: blank (w/o pyrrole).
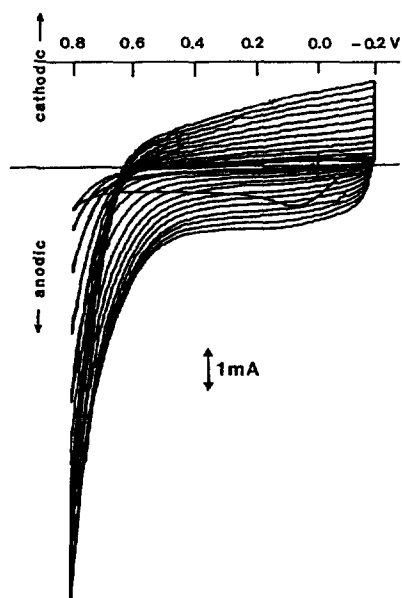
Figure 2. Repeated cyclic voltammograms of stainless steel in aqueous 1.0 M HNO₃ containing 50 mM pyrrole. Scan rate: 100 mV/sec.
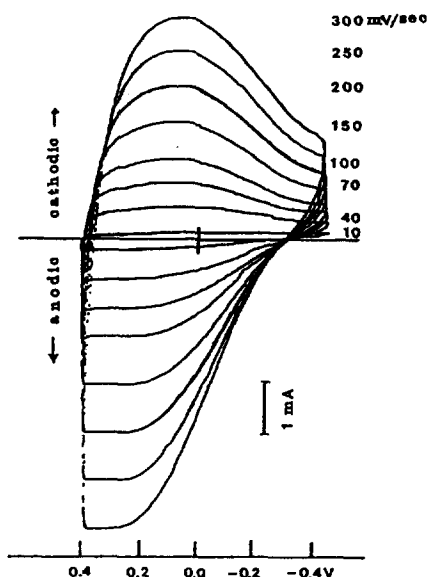

Figure 3. Cyclic voltammogram of polypyrrole coated Cr electrode in aqueous 1.0 M HNO₃ at various scan rate.

Figure 4. pH responses of (▲) PPy coated Pt, (▼) PPy coated stainless steel, (●) PPy coated Cr, and (■) glass electrodes using a Ag/AgCl reference electrode.

Table 1. Nernstian slopes and response times for PPy coated metal electrodes and for a typical glass electrode

	Pt	SS306	Cr	Ta	Nb	Zircaloy	Glass* Electrode
Nernstian Slope (mV/pH)	−58.1	−51.5	−51.7	−51.7	−52.6	−51.0	−59.1
Response Time (Sec)	220	257	250	203	222	380	23.8

*Horiba model 6326 glass electrode.

peaks discernible in the blank near 0.20 V for stainless steel and 0.12 V for Nb in Figure 1 are due to the oxidation of metals. The oxidation peaks disappeared from the second scan. (see Figure 2) Oxidation current around 0.12 V appeared from the second sweep and coninuously grew with cycles as typically shown for stainless steel in Figure 2. The currents near 0.20 V and 0.00 V are attributed to the oxidation and reduction of polypyrrole, respectively, which was confirmed by observing no further increase in current of a polypyrrole coated Pt in pyrrole free 1.0 M HNO₃ solution.

We measured the cyclic voltammograms of PPy in aqueous 1.0 M HNO₃ over the potential range from −0.4 V to 0.4
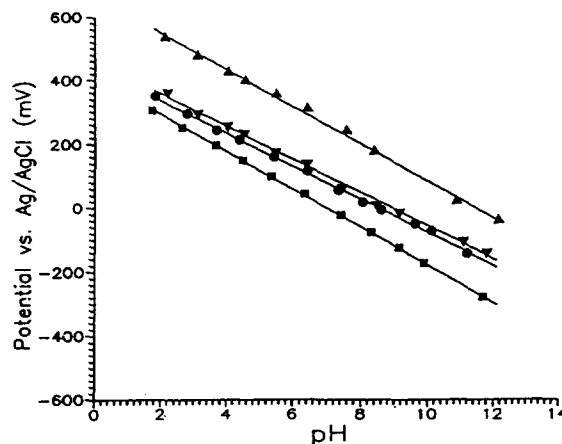
V at 100 mV/sec. As shown typically in Figure 3 with the PPy coated Cr, the cyclic voltammogram shows broad oxidation and redution peaks of PPy at various scan rates. The PPy coated Pt, stainless steel and Nb behaved similarly. However, for Ta and zircaloy, the peaks were not clearly observed. Since the difference in potential between the oxidation and reduction peaks is about 150 mV, the redox reaction of PPy seems to be not fast enough to maintain equilibrium concentrations of reactant and product as the potential is varied. Both i_p^a and i_p^c, the anodic peak current and the cathodic peak current, respectively, of all the PPy coated electrodes were proportional to the potential scan rate, indicating that the charge transport process within the PPy film on the metallic electrode is apparently adsorption controlled.

Figure 4 compares potentiometric responses of the PPy coated Pt, stainless steel, and Cr electrodes with that of a representative glass electrode, Horiba model 6326, over a pH range of about 2 to 12 at ionic strength of 0.10 M. Under the condition the potentiometric responses to hydronium ion are confirmed to be Nernstian with slopes of 58.1 mV and 59.1 mV, respectively, for the PPy modified Pt electrode and the glass electrode. Both of the slopes are within 2% of the expected value at 25 °C in agreement with the previous results.[10,14] The slopes of potential responses measured over the same pH range for the other PPy coated metal electrodes

Notes

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are summarized in Table 1. As can be seen from the table, the metal electrodes show the slopes of 50-52 mV/pH, which are about 14-11% lower than the expected value. The correlation coefficients of the linearity were better than 0.998 for all PPy modified electrodes.

The cause of the potential response has not been widely studied since Eq. (1) below was proposed. However, it is likely that the equilibrium of the acidic proton in the oxidized PPy in Eq. (1) leads to the appearance of a potential drop across the PPy layer. When the solution pH is changed, the dissociation equilibrium in Eq. (1) shifts. That is plausibly why the concentration of the charged PPy molecules and the associated potential drop changes. This dependence of the potential response on pH may be analogous to the dependence of the flat band potential of oxide semiconductors versus pH,[16] where hydroxyl groups on the surface dissociate in accordance with the ionization equation. The discrepancy in the Nernstian slope among metals appears to be caused by the morphology of PPy which changes depending on the surface conditions of an oxide-covered substrate. The morphology will affect the equilibrium in Eq. (1).
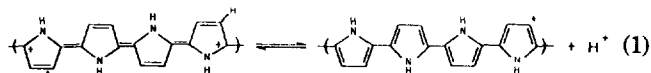

$$+ H^+ \quad (1)$$

Table 1 also provides the response times averaged over the pH range studied. Response time is defined here as the time required for the voltage change to be less than 1 mV/60 sec. The response times of the PPy coated metal electrodes are longer than that of the glass electrode, implying most likely that it takes longer for the reaction in Eq. (1) to become equilibrated within PPy. This is attributed to the decrease in the electron transfer rate across the oxide layer which was formed prior to PPy. The variation in response times among metals reflects the difference in morphology of PPy on each substrate.

It is concluded that well-adhering polypyrrole layers are formed on stainless steel, Cr, Ta, Nb, and zircaloy electrodes in aqueous nitric acid. The PPy coated metal electrodes are utilizable as potentiometric sensors for hydronium ion.[10]

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Metal Ion Catalyzed Aquation of *cis*-bis(methylmalonato)diaquochromate(III)[(1)]

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Isomerization and aquation of chromium(III) oxalate and chromium(III) malonate have been extensively studied.[2~23] We[22,23] reported recently the results of catalytic effect of metal ions on the aquations of *cis*-bis(oxalato)diaquochromate (III), *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ and *cis*-bis(malonato)-diaquochromate(III), *cis*-$Cr(C_3H_2O_4)_2(H_2O)_2$ and suggested the ring-opening process as the rate determining step to account for the metal ion-catalyzed aquation pathway. We extend the study on the metal-ion catalysis of the aquation of chromium (III) methylmalonate complexes. We have chosen Cu(II), Al (III) and VO^{2+} ions as potential catalytic cations since this metal ions have large affinity toward dicarboxylate anions.

Experimentals

Reagents. Potassium *cis*-bis(methylmalonato)diaquochromate(III), $KCr(C_4H_4O_2)_2(H_2O)_2$ was prepared from postassium dichromate and methylmalonic acid as described by Palmer.[24] Chromium content was determined by conversion of chromium(III) complexes to CrO_4^{2-} with alkaline peroxide, followed by spectrophotometric analysis of the CrO_4^{2-} produced ($\varepsilon_{373} = 4815$).[25] The stock solutions of cations used as catalysts were prepared from the nitrate, sulfate or perchlorate salts of corresponding cations. The solutions were analyzed by complexometric titrations employing disodium salt of ethylenediaminetetraacetic acid as the titration agent.[26] Water used in all the reactions was doubly distilled and sod-