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Simultaneous Formation of a Polypyrrole Film and a Tantalum Oxide Layer by Electrochemical Oxidation

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Electropolymerization of pyrrole on tantalum (Ta) electrodes was carried out in Britton-Robinson buffer solutions containing 0.1 M (1 M=1 mol dm^{-3}) potassium chloride (KCl) under galvanostatic conditions. A polypyrrole (PPy) film and a tantalum oxide (Ta_2O_5) layer are formed on a Ta electrode by one electrochemical oxidation process. The conditions of this simultaneous formation were investigated in respect with the current density, pyrrole concentration, pH, and total charge. Under certain conditions ([py]=0.5 M, pH=1.8, current density=3.5 mA cm^{-2}, charge 1 C), a 5.6 μm thick PPy film was efficiently formed on a homogeneous 45 nm thick Ta_2O_5 layer.

During the last decade electrical conducting polymers have been widely studied in order to apply them to electronic devices, such as electrochromic displays, rechargeable batteries, transistors, and capacitors.$^{1-6)}$ Polypyrrole (PPy), which can be easily prepared by electropolymerization, is a representative conductive polymer with high electronic conductivity and stability.$^{7,8)}$ Particularly, the application of PPy films to capacitors has been extensively studied.$^{9,10)}$ However, it is generally considered to be difficult to form a PPy film electrochemically on the surface of dielectric materials, such as aluminum oxide (Al_2O_3) and tantalum oxide (Ta_2O_5). Therefore, in a Ta (or aluminum) solid electrolytic capacitor, PPy formed previously on a dielectric layer by chemical polymerization is used as an electrode for the electropolymerization of pyrrole.

Tantalum (Ta) is known to be oxidized in aqueous media,$^{11)}$ as follows:

$$2Ta + 5H_2O = Ta_2O_5 + 10H^+ + 10e^- \qquad (1)$$

Metal Ta, which appears to be a base metal, tends to be covered with a oxide layer at all pH's.$^{12)}$ Since the Ta_2O_5 layer screens the Ta from immediate contact with an aqueous solution, a continuous formation of Ta_2O_5 results from the reaction of oxygen ions in an aqueous electrolyte with Ta ions migrating through the underlying oxide layer from bulk Ta.$^{13)}$

We reported previously that a PPy film could be electrochemically prepared on a Ta electrode in an organic solution.$^{14)}$ Recently, we found that the PPy film and a Ta_2O_5 layer could be simultaneously prepared on a Ta electrode in aqueous electrolyte solutions under galvanostatic conditions. This paper describes the formation profiles of the PPy/Ta_2O_5/Ta system and optimum conditions for the formation of the PPy/Ta_2O_5/Ta system.

Experimental

Materials. Electrolyte solutions were prepared from Britton–Robinson buffer solutions, pyrrole (Tokyo Kasei Ltd.) and potassium chloride (KCl: Kanto Chemical Co.). The Britton–Robinson buffer solutions (pH 1.8—12) comprised 0.04 M (1 M=1 mol dm^{-3}) of phosphoric acid, 0.04 M of acetic acid, 0.04 M of boric acid, and 0.2 M sodium hydroxide. Pyrrole was purified twice by distillation under a nitrogen atmosphere. Water was distilled three times and deionized.

Electropolymerization of Pyrrole. Electropolymerization of pyrrole was carried out galvanostatically using a dual potentiogalvanostat (Nikko Keisoku NPGS-301) under a nitrogen atmosphere. The charge passed during the polymerization was meaured with a digital coulomb meter (Nikko Keisoku NDCM-1). The polymerization of pyrrole and the oxidation of Ta were studied in the Britton–Robinson buffer solutions containing 0.1 M KCl by cyclic voltammetry using a Solartron 1286 electrochemical interface (Schlumberger Technologies).

A Teflon–Ta (or Pt) disk electrode (ϕ=6 mm), a saturated calomel electrode (SCE), and a Pt wire were used as a working electrode, a reference electrode, and a counter electrode, respectively. Before the electropolymerization of pyrrole, Pt and Ta electrodes were polished with a sheet of abrasive paper (E-300: Koyo-sha Co.), and then with alumina powder (1 μm, 0.3 μm), on the finest quality microcloth (Buehler Ltd.).

Measurements. The PPy films formed by the electropolymerization of pyrrole were first rinsed with distilled water, followed by acetone, and then dried in a desiccator for one day. They were peeled off the electrodes and dried in vacuo without heating. The thickness of the films was determined by a scanning electron microscope (JEOL JSM-T20). On the other hand, the thickness of Ta_2O_5 layers was calculated from the capacitance obtained from an alternating current (ac) impedance method (1—5×10^5 Hz) under potentiostatic control (Solartron 1286 electrochemical interface).$^{15)}$ Impedance spectra were recorded on a Solartron 1255 frequency response analyzer. A Pt wire was used as a counter electrode.

The electrical conductivity of PPy films was measured by a four-probes method based on the van der Pauw theory at room temperature after being peeled off the electrodes.$^{16)}$

Results and Discussion

Cyclic Voltammetry of the Pyrrole Monomer. Figure 1a shows cyclic voltammograms of the 0.05 M pyrrole monomer in Britton–Robinson buffer solutions con-

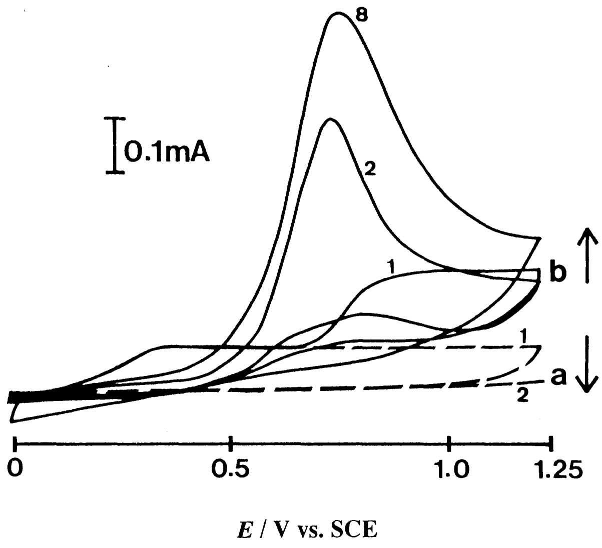

Fig. 1. Cyclic voltammograms of pyrrole on a Ta electrode (ϕ=6 mm) in a 0.1 M KCl aq solution: [Py]=0.05 M(a); 0.5 M(b). Scan rate=0.1 V s^{-1}.

taining 0.1 M KCl with Teflon–Ta disk electrodes. A rapid current decrease was observed in the second sweep, indicating that the Ta electrode was immediately oxidized during the first sweep, and that no PPy film was virtually formed under low pyrrole concentrations.

In contrast, at higher concentration (0.5 M) of pyrrole, the oxidation peak current gradually increased with cyclic number (Fig. 1b), even though the typical behavior of Ta_2O_5 formation was also observed during the early stage of the first sweep. This is because the electrode potential reaches the oxidation potential of pyrrole before the Ta electrode is sufficiently oxidized.[17] That is, the polymerization of pyrrole proceeds due to a direct electron transfer between Ta and the electrolyte through very thin Ta_2O_5 layers, i.e., electron tunneling.[18]

Effect of the Current Density on the Oxidation of Pyrrole and Ta. Electropolymerization of pyrrole was carried out on a Ta electrode galvanostatically in a Britton–Robinson buffer solution containing 0.1 M KCl. The potential–time characteristics of galvanostatic electrolysis are shown in Fig. 2. In the absence of pyrrole, the electrolysis of bare Ta electrodes increased the potential linearly with time, indicating the growth of Ta_2O_5 layers.[19] The slope of the lines increases with current density. The growth rate of the Ta_2O_5 thickness per potential increase was reported to be 1.76 nm V^{-1}.[20–22] Ta_2O_5 grows due to the high-field ion migration of Ta ions outwards and oxygen ions inwards.[23]

Different profiles were observed in the presence of 0.5 M pyrrole. Firstly, the potential rises in the same way as in the absence of pyrrole, and then show a plateau. This plateau indicates the formation of PPy on Ta_2O_5. The structure of PPy/Ta_2O_5/Ta was also characterized by ESCA. Firstly, the peaks of N_{1s}, C_{1s}, and O_{1s} appeared at 399.8, 285.1, and 532.1 eV, respectively; these coincide with the typical PPy formed on a Pt electrode. After etching of the PPy film, the Ta_2O_5 layer (Ta–O binding energy: 26.7 eV) was confirmed under the PPy film.[24]

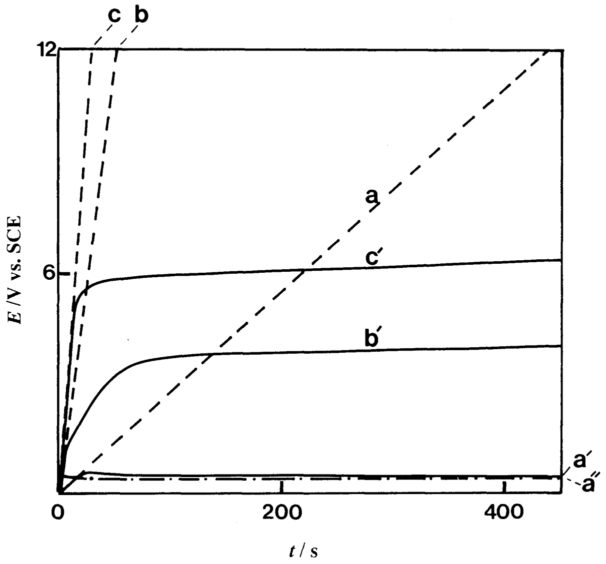

Fig. 2. Potential-time characteristics of galvanostatic electrolysis of electrodes in a 0.1 M KCl aq solution at various current densities: Ta in the absence of pyrrole (----); Ta (——) and Pt (—•—) in the presence of 0.5 M pyrrole; current density (mA cm^{-2})=0.1 (a, a′, a″), 0.5 (b, b′), 1.0 (c, c′).

The oxidation of Ta electrodes was clarified to proceed more preferentially than that of pyrrole during the initial stage. This is because the oxidation potential of Ta into Ta_2O_5 (−0.81 V)[12] is much lower than that of the pyrrole monomer (+0.8 V to + 1.1 V vs. SCE in aqueous solutions).[25] It is noted that at a current density of 0.1 mA cm^{-2}, the electropolymerization of pyrrole proceeds at nearly the same potential (0.47 V vs. SCE) as that on the Pt electrode (Fig. 2a″). This is because Ta_2O_5 below 10 nm thick behaves like a n-type semiconductor due to oxygen deficiencies;[20] further, electrostatic interaction occurs between Ta electrodes and the electrolyte, which leads to direct electron tunneling.[18]

At a current density higher than 0.1 mA cm^{-2}, the electrode potential gradually increases with the growth of Ta_2O_5, because of the insulating property of thicker Ta_2O_5, and the fact that the rate of Ta_2O_5 formation during the initial stage doesn't depend on the presence of pyrrole, but increases with the applied current density. At a potential determined by the applied current density, the polymerization of pyrrole becomes predominant. The electronic conduction of thick Ta_2O_5 can be interpreted in terms of the space-charge limited mechanism, which is the conduction mechanism of insulating Ta_2O_5 films thicker than 30 nm in the high field-region.[18,26] The conduction depends critically on the defects of nonstoichiometrical Ta_2O_5, which eventually acts as electronic trapping centers. According to the Ikonopisov model of an avalanche,[27] electrons are injected from the electrolyte to the oxide conduction band. These incorporated anions result in the formation of traps which are in electronic equilibrium with the electrolyte. The electrons are thermally excited from the traps into the conduction band, and electronic equilibrium is maintained by a continuous injection of electrons from the electrolyte. These electrons are accelerated by the high anodization electric field, producing avalanches by impact ionization; this causes a breakdown when a certain critical current is reached. As a result, the current passing through the Ta_2O_5 layer is entirely electronic, and is referred to as the leakage current.[28,29] That is, the polymerization of pyrrole on a Ta_2O_5 layer is possible by flowing an electronic current in the Ta/Ta_2O_5/electrolyte system.

Figure 3 summarizes the dependences of the thicknesses of the PPy film and the Ta_2O_5 layer on the current density (i_d) applied to the polymerization of pyrrole on Ta. In this case, electropolymerization was carried out in a 0.5 M pyrrole buffer solution (pH 1.8) containing 0.1 M KCl; the charge passed during polymerization was 1.0 C. The thickness of the PPy film formed on Ta electrodes decreased drastically upon increasing the current density, since part of the charge was consumed for the formation of Ta_2O_5; this is understandable from the results given in Fig. 2. For current densities below 3 mA cm^{-2}, the formation of Ta_2O_5 is restrained due to the predominant formation of PPy after formation of a thin Ta_2O_5 layer. In contrast, the PPy film does not form in current densities higher than 5 mA cm^{-2}, because of the formation of a Ta_2O_5 layer thicker than 50 nm, which behaves like insulators. Therefore, applied current densities from 3 to 5 mA cm^{-2} provide both a PPy film and an insulating 40—50 nm thick Ta_2O_5 layer. On the other hand, when Pt was used as an electrode instead of Ta, the thickness of the PPy films was not influenced by the current density, since no oxidation of the electrode took place.

Effect of Pyrrole Concentration on the Oxidation of Pyrrole and Ta. The dependences of the thickness of the PPy film and the Ta_2O_5 layer on the pyrrole concentration used for the polymerization of pyrrole on Ta are shown in Fig. 4. In this case, electropolymerization was carried out in 0.1 M KCl solutions (pH 1.8) with different pyrrole concentrations under galvanostatic conditions

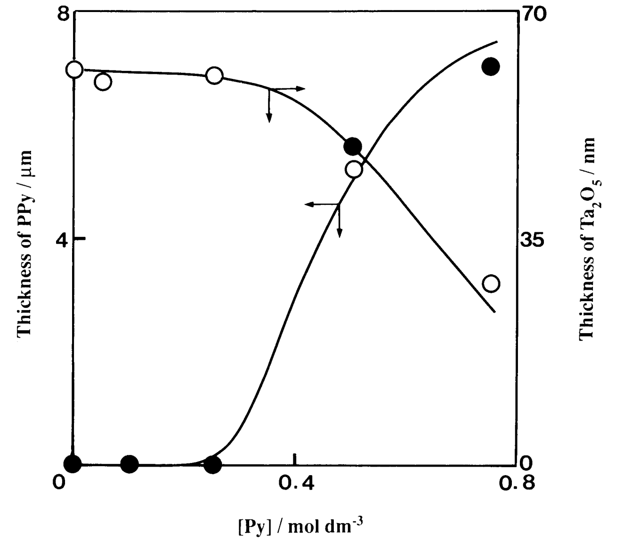

Fig. 4. Effect of the pyrrole concentration on the simultaneous formation of PPy and Ta_2O_5: PPy (●); Ta_2O_5 (○). Conditions: i_d 3.5 mA cm^{-2}; pH 1.8; Charge 1C.

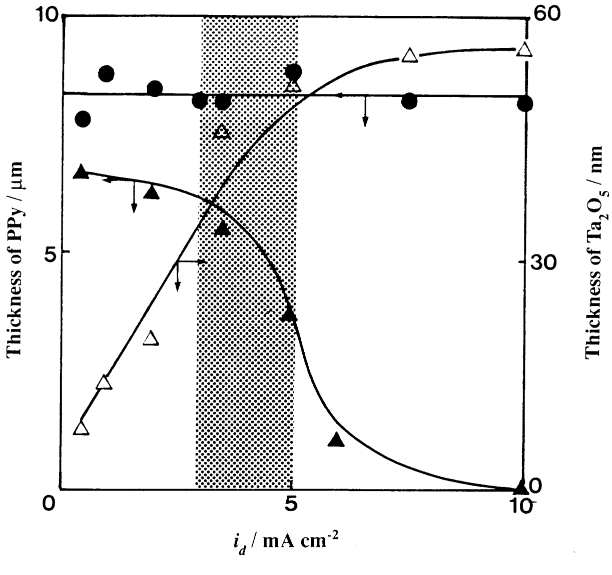

Fig. 3. Effect of the current density on the simultaneous formation of PPy and Ta_2O_5: Pt/PPy (●); Ta/PPy (▲); Ta_2O_5 (△). Conditions: [Py] 0.5 M; pH 1.8; Charge 1C.

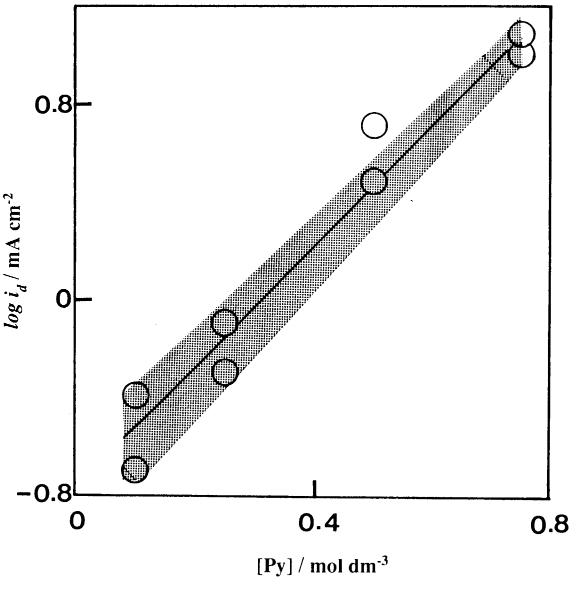

Fig. 5. Relationship between [Py] and the current density during the simultaneous formation of PPy and Ta_2O_5. Conditions: Charge 1C; pH 1.8.

(i_d=3.5 mA cm^{-2}); the charge passed during polymerization was 1.0 C. The thickness of the PPy film formed on the Ta electrode started to increase sharply from a pyrrole concentration of 0.3 M. In contrast, the thickness of Ta_2O_5 started to gradually decrease from the same concentration. These results indicate that PPy formation on Ta_2O_5 is influenced by the pyrrole concentration, as also shown in Fig. 1. Since the oxidative potential of pyrrole at the surface of Ta_2O_5 would be lower with increasing pyrrole concentration, the polymerization of pyrrole proceeds dominantly at a lower potential of the electrode, resulting in the growth of a thinner Ta_2O_5 layer.

Figure 5 summarizes the optimum region of the current density and the pyrrole concentration for the simultaneous formation of both the PPy film and the Ta_2O_5 layer. If the current density is higher, or the pyrrole concentration is lower, than this region, the PPy film is not formed because of the formation of a thick Ta_2O_5 layer, which behaves like an insulator. When the current density is lower, or the pyrrole concentration is higher, than this region, the formation of Ta_2O_5 is restrained because of the predominant formation of PPy after the formation of a thin Ta_2O_5 layer (Fig. 3). The thickness of the Ta_2O_5 layer which is formed in this region is approximately 30—50 nm; the color of which is blue.

Effect of pH on the Oxidation of Pyrrole and Ta. The influence of pH upon the electropolymerization of pyrrole on a Ta electrode was studied, and is shown in Fig. 6. In this case, polymerization was carried out under galvanostatic conditions (i_d=3.5 mA cm^{-2}) in aqueous buffer solutions of 0.5 M pyrrole containing 0.1 M KCl. Only a few stains of PPy appeared on the surface of a Ta electrode when the solution pH was above 3.5. The polymerization, however, proceeded efficiently below this pH.

These phenomena can be explained in terms of the following experiments. Figure 7 shows the effect of pH on the amount of charge passed during the first scan in cyclic voltammetry during the electrooxidation of Ta and the electropolymerization of pyrrole (0.05 M) on a Pt

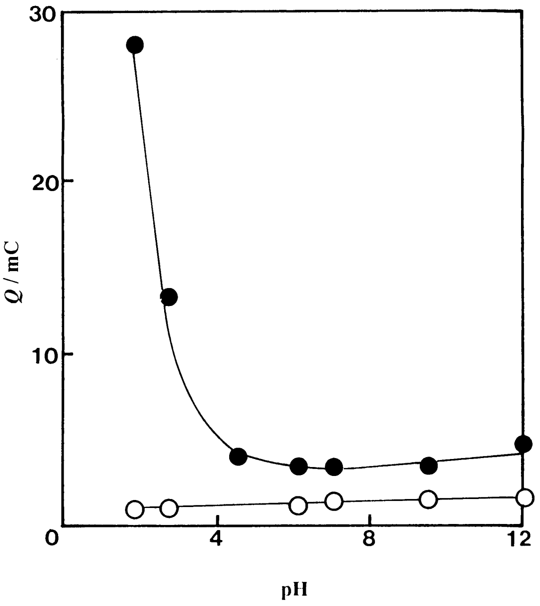

Fig. 7. Effect of pH on the amount of charge passed during the first scan in cyclic voltammetry for the oxidation of a bare Ta electrode (○) and pyrrole monomer (●).

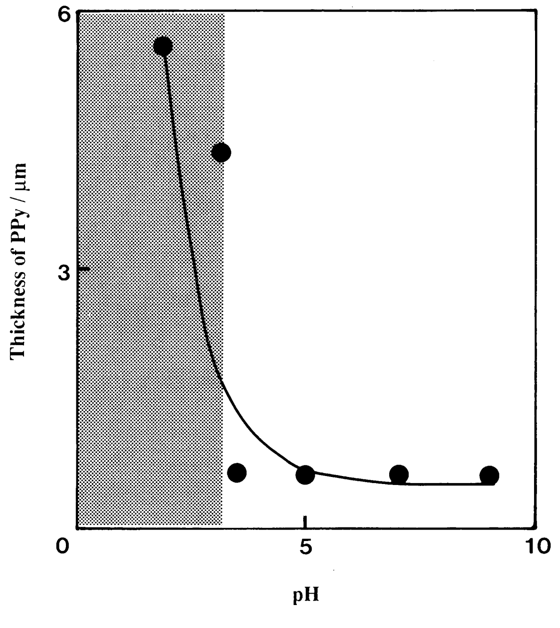

Fig. 6. Effect of pH on the electropolymerization of pyrrole using Ta electrodes under galvanostatic conditions: i_d 3.5 mA cm^{-2}; [Py] 0.5 M; Charge 1C.

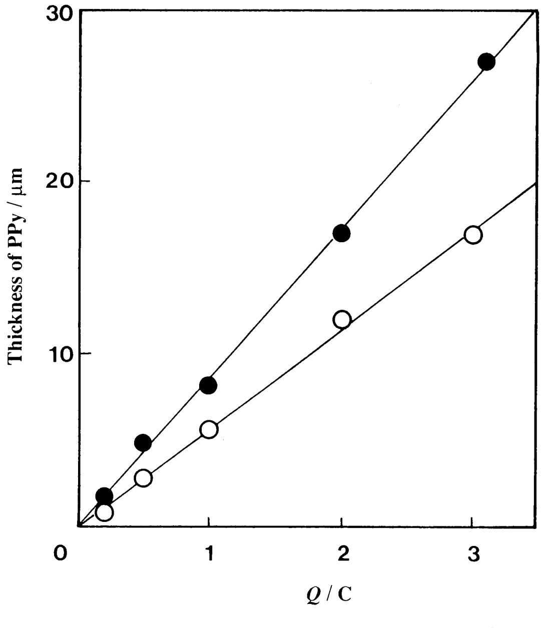

Fig. 8. Relationship between the amount of charge passed during the electropolymerization of pyrrole and the thickness of the resulting PPy films: Pt (●); Ta (○). Conditions: [Py] 0.5 M; pH 1.8; i_d 3.5 mA cm^{-2}.

electrode. The amount of charge used for the electro-oxidation of Ta is not greatly influenced by pH. The amount of charge used for the polymerization of pyrrole, however, increases significantly below pH 3.5. This corresponds well with the pH dependence of the thickness of PPy on a Ta electrode (Fig. 6). It is considered that pyrrole, which was protonated to form a cation radical, should start polymerization preferentially before it transfers an electron to the electrode. Therefore, pyrrole can feasibly polymerize electrochemically at low pH.[30)]

Charge for the Preparation of PPy and Ta_2O_5. Figure 8 shows the relationship between the charge passed during the electropolymerization of pyrrole and the thickness of the resulting PPy films. As expected, the thickness of PPy films formed on Pt electrodes increases linearly with the amount of charge. The PPy films on Ta electrodes, however, are thinner than those on Pt electrodes.

For example, the thicknesses of PPy films formed on Pt and Ta electrodes under the same conditions (1 C) were 8.1 and 5.6 μm, respectively. The difference in the thickness (2.5 μm) can be interpreted in terms of the charge (315 mC) consumed for the formation of a Ta_2O_5 layer. The thickness of the Ta_2O_5 layer can be estimated from

$$\Delta d = QV_M/AF = 0.476\ (Q/\text{mC cm}^{-2})\ \text{nm},^{20)} \qquad (2)$$

where Q is the charge (mC cm^{-2}), V_M is the molalr volume (50.6 cm^3 mol^{-1}), F is 96490 C mol^{-1}, and A is the area of electrode (0.2826 cm^2). The thickness of the Ta_2O_5 layer formed from a charge of 315 mC was calculated to be 42 nm. The thickness of the Ta_2O_5 layer measured from the ac impedance method is 45 nm, which coincides well with the calculated value.

Elelctrical Conductivity of a PPy Film. The electrical conductivities of PPy films formed on Ta_2O_5 layers at various pyrrole concentrations were measured at room temperature. As shown in Fig. 9, the electrical conductivity increases with the pyrrole concentration, showing a maximum value (40 S cm^{-1}) at a concentration of 0.5 M. This trend corresponds well with the previous results reported by Yamamura et al.[31)] They explained that at higher concentrations, which required a higher current density for the simultaneous formation of PPy and Ta_2O_5, the conductivity decreased because of a side reaction due to an over voltage; a decrease took place in the conductivity at lower concentrations, i.e., the lower current density could be explained in terms of a side reaction due to prolonged polymerization. As-grown PPy films show 10—40 S cm^{-1}, the same electrical conductivity as those on Pt electrodes. These results indicate that a PPy film prepared on Ta_2O_5 is the same as a film on Pt.

In conclusion, conductive PPy films could be prepared on insulating Ta_2O_5 layers under galvanostatic conditions. The formation of PPy film is drastically influenced by the current density, pyrrole concentration and pH. Under certain conditions ([Py]=0.5 M, pH 1.8, current density=3.5 mA cm^{-2}, charge 1 C), polymerization proceeds effectively to form a PPy film on the Ta_2O_5 layer (40—50 nm) formed during the initial stage. At the lower current density, lower pH and higher concentration of pyrrole in comparison with the conditions, the growth of the Ta_2O_5 was restrained because of the predominant formation of PPy. At a higher current density, higher pH or lower concentration of pyrrole, no PPy film was formed, because of the formation of Ta_2O_5 layers thicker than 50 nm, which behaved like an insulator. The electropolymerization of pyrrole on a Ta electrode from Britton–Robinson buffer solutions leads to the formation of a sandwich-like structure of PPy/Ta_2O_5/Ta, which can be regarded as being a capacitor.

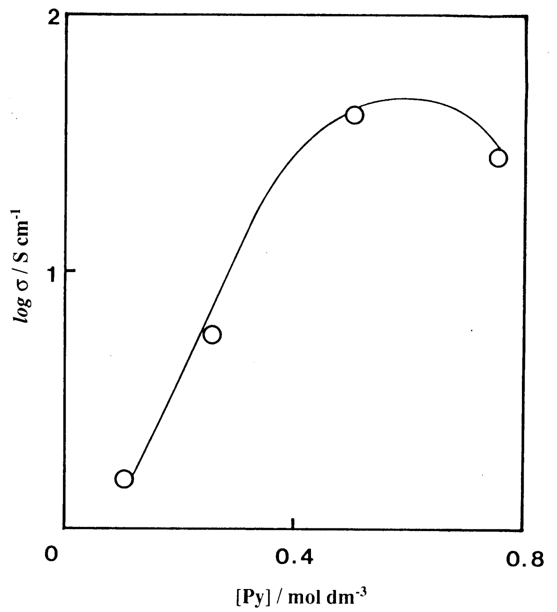

Fig. 9. Effect of [Py] on the conductivity of the resulting PPy films. Conditions: Charge 1C; pH 1.8.

References

1) G. K. Chandler and D. Pletcher, *Chem. Soc., Spec. Period. Rep. Electrochem.*, **10**, 117 (1985).

2) H. Yoneyama, K. Wakamoto, and H. Tamura, *J. Electrochem. Soc.*, **132**, 2414 (1985).

3) K. Kaneto, M. Maxfield, D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger, *J. Chem. Soc., Faraday Trans.*, **78**, 3417 (1982).

4) J. W. Thackeray, H. S. White, and M. S. Wrighton, *J. Phys. Chem.*, **89**, 5133 (1985).

5) K. Yamamoto, T. Asada, H. Nishide, and E. Tsuchida, *Bull. Chem. Soc. Jpn.*, **61**, 1731 (1987).

6) K. Yamamoto, T. Asada, H. Nishide, and E. Tsuchida, *Bull. Chem. Soc. Jpn.*, **63**, 1211 (1990).

7) D. S. Maddison and J. Unsworth, *Synth. Met.*, **30**, 47 (1989).

8) F. T. A. Vork and L. J. Janssen, *Electrochim. Acta,* **33**, 1513 (1988).

9) R. Erlandsson, O. Inganas, I. Lundstrom, and W. R. Salaneck, *Synth. Met,,* **10**, 303 (1985).

10) Y. Kudoh, S. Tsuchiya, T. Kojima, M. Fuluyama, and S. Yoshimura, *Synth. Met.,* **41—43**, 1133 (1991).

11) L. L. Odynets, *Elelctrokimiya,* **20**, 453 (1984).

12) H. V. K. Udupa and V. K. Venkatesan, "Encyclopedia of Electrochemistry of the Elements," ed by A. J. Bard, Marcel Dekker, New York (1974), Vol. 2, p. 60.

13) W. Wilhelmsen, *Electrochim. Acta,* **33**, 63 (1988).

14) K. Yamamoto, Y. S. Park, S. Takeoka, and E. Tsuchida, *J. Electroanal. Chem.,* **318**, 171 (1991).

15) B. Van Der Linden, H. Terryn, and J. Vereedcen, *J. Appl. Electrochem.,* **20**, 798 (1990).

16) L. J. Van der Pauw, *Philips Tech. Rev.,* **20**, 220 (1958/1959).

17) K. M. Cheung, D. Bloor, and G. C. Stevens, *Polymer,* **29**, 1709 (1988).

18) M. Metikos-hukovic and M. Ceraj-ceric, *Thin Solid Films,* **145**, 39 (1986).

19) J. M. Albella, I. Montero, and J. M. Martinezduart, *Thin Solid Films,* **125**, 57 (1985).

20) V. Macagno and J. W. Schultze, *J. Electroanal. Chem.,* **180**, 157 (1984).

21) J. Klerer, *J. Electrochem. Soc.,* **112**, 896 (1965).

22) D. J. Smith and L. Young, *Thin Solid Films,* **101**, 11 (1983).

23) L. Young, "Anodic Oxide Films," Academic Press, London (1961).

24) Y. S. Park, K. Yamamoto, S. Takeoka, and E. Tsuchida, *Polym. Adv. Tech.,* (1992), in press.

25) S. Asavapiriyanont, G. K. Chandler, G. A. Gunawardena, and D. Pletcher, *J. Electroanal. Chem.,* **177**, 229 (1984).

26) I. Montero, J. M. Albella, C. Ortega, and J. Siejka, *Thin Solid Films,* **167**, 95 (1988).

27) S. Ikonopisov, *Electrochim. Acta,* **22**, 1077 (1977).

28) S. Ikonopisov and N. Elenkov, *J. Electroanal. Chem.,* **86**, 105 (1978).

29) S. Ikonopisov and N. Elenkov, *J. Electroanal. Chem.,* **88**, 417 (1978).

30) R. Qian, Q. Pei, and Z. Huang, *Makromol. Chem.,* **192**, 1263 (1991).

31) M. Yamamura, T. Hagiwara, and K. Iwata, *Synth. Met.,* **26**, 209 (1988).