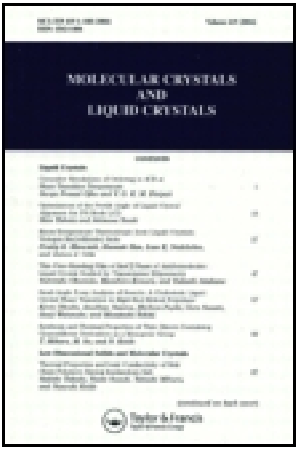

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In situ FORMATION OF PPy/Ta_2O_5/Ta STRUCTURE BY ELECTRO-POLYMERIZATION AND ITS ELECTRICAL PROPERTIES

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Abstract Both PPy film and Ta_2O_5 layer are simultaneously formed on Ta-electrode by one process of electrical oxidation in an aqueous solution. Preparation of the structure (PPy/Ta_2O_5/Ta) can also takes place by the electrolysis using Ta-electrode on which PPy is formed previously by electropolymerization. Since PPy film obtained by the former method has higher electric conductivity (110 S/cm) and better adhesion than the later, (PPy/Ta_2O_5/Ta)structure formed simultaneously is confirmed better electrical properties as a capacitor.

INTRODUCTION

Base metals such as tantalum(Ta), iron, and aluminum tend to form insulating oxide films or to dissolute anodically from the surface of these electrodes, giving rise to narrow potential windows. Therefore, these metals have had less attention as electrode materials in the electropolymerization of pyrrole. However, some attempts using base metal electrodes have been reported recently.[1-3] Since the tantalum oxide(Ta_2O_5) layer screens the Ta immediately from contact with an aqueous solution at all pH's, the 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 the bulk Ta.[4] Owing to outstanding dielectric characteristics such as the low leakage current(LC), Ta_2O_5 is widely used in electronic devices, such as electrolytic capacitors, MOS transistors, and solar cells.

However, it is generally considered to be difficult to form a PPy film electrochemically on the surface of such dielectric materials. Therefore, in making a Ta (or aluminum) solid electrolytic capacitor, PPy formed previously on a dielectric layer by chemical polymerization is used as an electrode for the subsequent electropolymerization of pyrrole.[5] By attempting the electropolymerization of pyrrole using the base metals such as Ta, PPy films were found to be formed on Ta electrodes in a similar manner to those on Pt electrodes under some conditions,[6] while, only Ta_2O_5 layers were formed under other conditions. Interestingly, three layer-structure of PPy/Ta_2O_5/Ta was obtained under the intermediate conditions of those two conditions.[7,8] Furthermore, the three layer-structure can also be obtained from the galvanostatic electrolysis of the PPy film previously formed on the Ta electrode by electropolymerization.[9]

In this paper, optimum conditions of the formation of the PPy/Ta_2O_5/Ta structure were summarized, and the properties of PPy and Ta_2O_5 obtained by one electrochemical oxidation process or two oxidation process were compared.

ELECTROPOLYMERIZATION OF PYRROLE ON A Ta ELECTRODE

Electropolymerization was carried out using Pt and Ta disk electrodes (6 mm ϕ) in an acetonitrile solution containing 0.1 M tetra-n-butylammonium perchlorate (TBAP) and pyrrole monomer (0.1 M) by cyclic voltammetry in the potential range from 0 to 1.5 V under a nitrogen atmosphere.

In electrolysis using a Ta electrode, the electropolymerization of pyrrole did not occur easily at low pyrrole concentrations (below 0.1 M) because a thin Ta_2O_5 layer insulates the surface of the Ta electrode. The insulating Ta_2O_5 was formed on the surface of the Ta electrode because the Ta electrode was oxidized with a small amount of water in acetonitrile. If the polymerization rate becomes larger than the formation rate of Ta_2O_5 with increasing the pyrrole concentration, PPy is readily formed on the Ta electrode. The PPy was thus prepared efficiently on a Ta electrode by electropolymerization in a high concentration of pyrrole. Polymerization proceeds because once-formed, conductive PPy acts as an electrode, similar to that on Pt.

Figure 1 shows that the redox charge is proportional to the charge for the PPy formation up to about 0.22 C. This indicates that active sites are formed continuously, corresponding to the amount of PPy. From Figure 1, the electropolymerization of PPy on Ta gives the same amount of PPy having the same electroactivity as that on Pt.

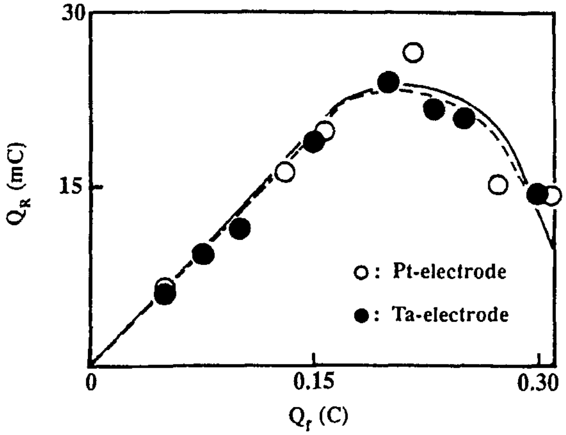

FIGURE 1. Relationship between the charge(Q_f) passing during the electropolymerization (0.1 M pyrrole) by cyclic voltammetry and the charge(Q_R) at a redox cycle of PPy films.

SIMULTANEOUS FORMATION OF A PPy FILM AND A Ta_2O_5 LAYER BY ELECTRICAL OXIDATION

Cyclic Voltammetry of Pyrrole Monomer

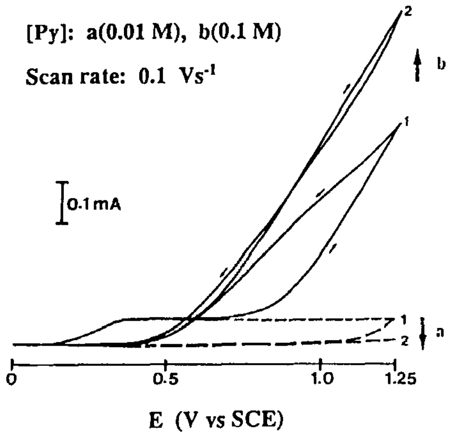

FIGURE 2. Cyclic voltammograms of pyrrole on Ta electrodes (6 mm ϕ) in 0.1 M TsONa aqueous solutions

Electropolymerization was carried out using Pt and Ta disk electrodes (6 mm ϕ) in aqueous pyrrole solutions containing 0.1 M p-toluenesulfonate(TsONa). As shown in Figure 2, at a lower concentration (0.01 M) of pyrrole, a rapid current decrease was observed in the second sweep, indicating that the Ta electrode was immediately oxidized during the first sweep and that virtually no PPy film was formed at such a low pyrrole concentration. In contrast, at a higher concentration (0.1 M) of pyrrole, the oxidation peak current gradually increased with cycle number (Figure 2(b)), even through the typical behavior of Ta_2O_5 formation was also observed during the early stage (0-0.72 V) of the first sweep. This is because the electrode potential reaches the oxidation potential of pyrrole before the Ta electrode is sufficiently oxidized.[2] That indicates that the polymerization of pyrrole proceeds due to direct electron transfer between Ta and the electrolyte through very a thin Ta_2O_5 layer, i.e., electron tunneling.[10]

As shown in Figure 3, at pyrrole concentrations lower than 0.1 M, the charge passing during the electrolysis was only used for the formation of Ta_2O_5, and was not used for the formation of PPy. With increasing the pyrrole concentration, the amount of formed PPy increased, while that of Ta_2O_5 decreased. Particularly, at pyrrole concentrations higher than 0.75 M, PPy was formed on Ta electrode with a little formation of Ta_2O_5. This is because pyrrole is readily oxidized and PPy films is formed on the thin oxidized layer of the electrode surface. Therefore, pyrrole concentrations of 0.1-0.5 M are required for the simultaneous formation of PPy and Ta_2O_5.

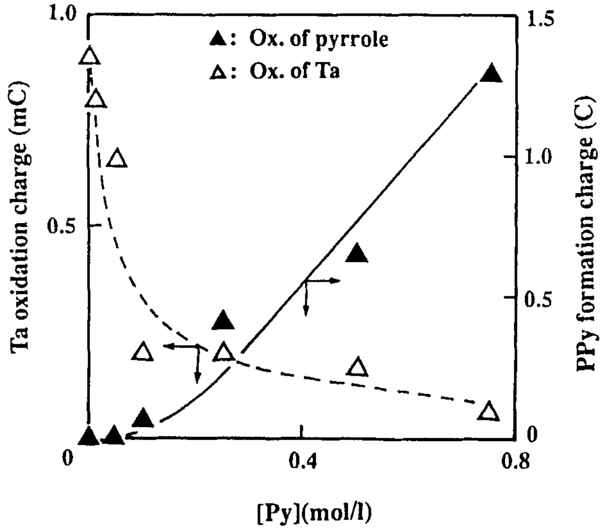

FIGURE 3. Effect of the pyrrole concentration(0.01-0.75 M) on the amount of the charge for the electropolymerization of pyrrole.

Effect of the Current Density and the Pyrrole Concentration on the Oxidation of Pyrrole and Ta.

In the absence of pyrrole (Figure 4, a, b, c), the potential of the galvanostatic electrolysis of bare Ta electrodes increased linearly with time, indicating the growth of Ta_2O_5 layers. The Ta_2O_5 thickness per potential increase was reported to be 1.76 nm V^{-1}.[11] The slope of the lines increased with the current density.

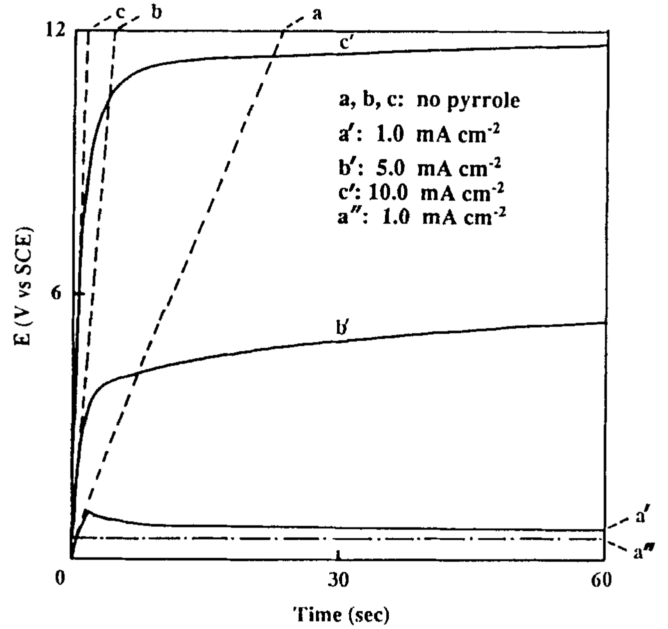

FIGURE 4. Potential-time characteristics of the galvanostatic electrolysis of Ta electrodes in aq. solutions containing 0.25 M pyrrole and 0.1 M TsONa at various current densities.

In the presence of 0.25 M pyrrole, the potential rose in the same way as in the absence of pyrrole at the initial stage of electrooxidation and then showed a plateau. This plateau is considered to be due to the formation of PPy on Ta_2O_5. The oxidation of a Ta electrode should proceed more preferentially than that of pyrrole during the initial stage because the oxidation potential of Ta to Ta_2O_5 (-0.81 V) is lower than that of the pyrrole monomer (+0.8 V to +1.1 V vs SCE in aqueous solutions).[12] It is noted that at a current density of 1 mA cm^{-2} the electropolymerization of pyrrole proceeded at nearly the same potential (0.6 V vs SCE) as that on a Pt electrode (Figure 4a″). This indicates that the polymerization of pyrrole is predominant at such a low current density because Ta_2O_5 below 10 nm thick would behave like *n*-type semiconductor due to oxygen deficiencies[11] or would allow to direct electron tunneling.[10]

Figure 5 shows the relationship between the amount of charge passing during the electropolymerization of pyrrole and the thickness of the resulting PPy films and Ta_2O_5 layers. The Ta_2O_5 layer was mainly formed at a low charge density below 5 C cm^{-2}, i.e., at the early stage of the electropolymerization. On the other hand, the PPy films grew gradually with the charge density. This indicates that pyrrole can be electropolymerized by flowing electronic current through the Ta_2O_5 layer by means of the galvanostatic conditions. The electronic conduction of the thick Ta_2O_5 layer can be interpreted in terms of the space-charge limited mechanism(the Ikonopisov model of an avalanche[13]), which is the conduction mechanism of insulating Ta_2O_5 films thicker than 30 nm in a high-field region.[10]

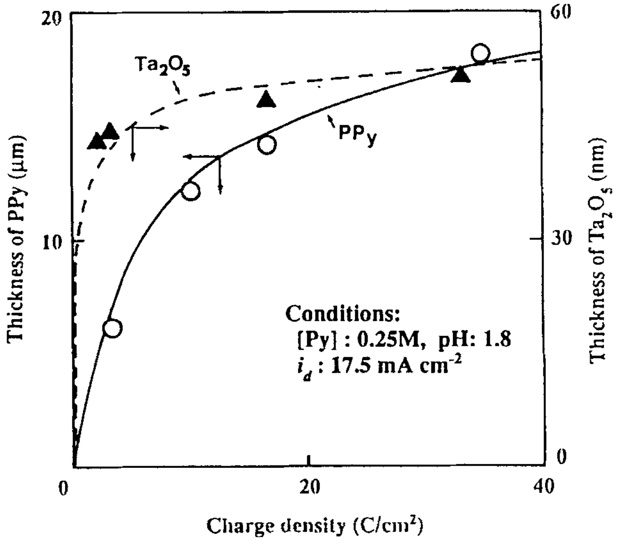

FIGURE 5. Relationship between the amount of charge passing during the electropolymerization of pyrrole and the thickness of the resulting PPy films(○) and Ta_2O_5 layers(▲). The thickness of the PPy is determined by SEM and that of the Ta_2O_5 layers is calculated from the capacitance.

Figure 6 summarizes the optimum region of the current density and the pyrrole concentration for the simultaneous formation of PPy and Ta_2O_5. 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 insulating Ta_2O_5 layer. 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. The thickness of the Ta_2O_5 layer which was formed in this region was approximately 30-50 nm; the color of which was blue.

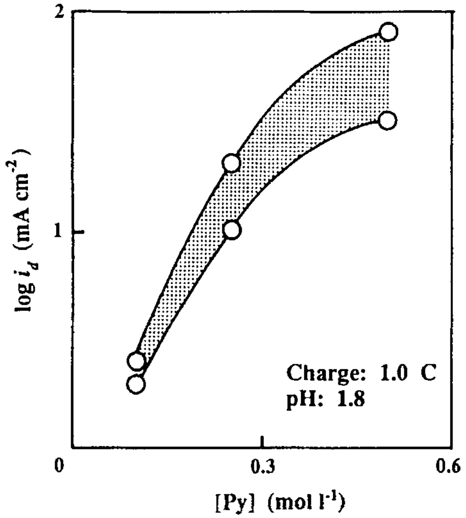

FIGURE 6. Optical conditions of [Py] and i_d for the simultaneous formation of PPy and Ta_2O_5.

OXIDATION OF Ta ELECTRODES COVERED WITH PPy(PPy/Ta)

Oxidation Behavior of PPy/Ta electrodes

Electropolymerization of pyrrole carried out in 0.2 M pyrrole aq. solutions(pH 1.8) by cyclic voltammetry method. The amount of charge passing during polymerization was 0.5 C. Figure 7(a) shows the oxidation behavior of a PPy(TsO$^-$)/Ta electrode at the current density of 120 μA cm^{-2}. The constant potential at about 0.7 V was observed in the initial region (A-B). After the potential-jump to ca. 5V (B-C), the potential started to rise steeply.

The control experiments were carried out using the Pt electrodes(Figure 7(b)). The potential (about 0.7 V) was constant at the initial region (A'-B') of the electrolysis. After potential-jump (B'-C'), the second plateau (about 1.5 V vs SCE) (C-D') appeared.[14] At the region of A'-B', the irreversible oxidation of PPy films is considered to occur by nucleophile(OH$^-$) attack to the pyrrole radical cations.[15] The potential jumps to the potential for the decomposition of solvent (the aqueous solution of 0.01 wt% phosphoric acid), and the decomposition of the solvent takes place at a C'-D' region. Therefore, in the case of the oxidation behavior of PPy/Ta electrode, the initial plateau of the potential(A-B) should be due to the oxidation of PPy, and the oxidation of Ta should start after the potential jump (B-C).

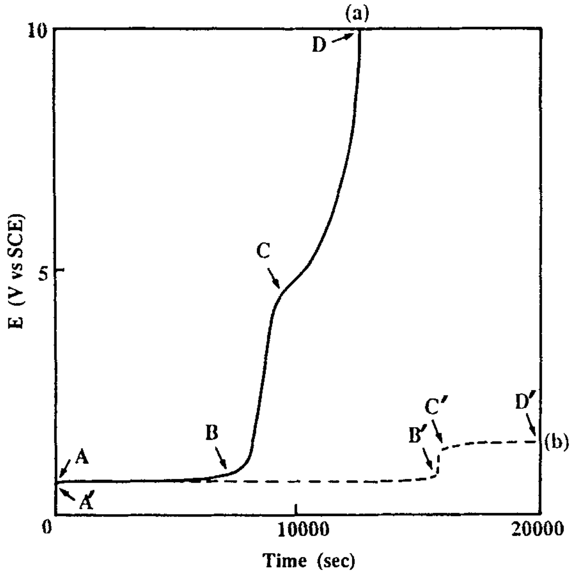

FIGURE 7. Oxidation behavior of Ta (a) and Pt (b) electrodes coated with PPy in the aqueous solution of 0.01 wt% phosphoric acid.

Structure of PPy(TsO⁻) Films

The structures of PPy were known to be aromatic forms in neutral or reduced states and quinoid forms in anion doped or oxidized states.[16] Therefore, the structure of the electropolymerized PPy film is considered to be the mixture of aromatic and quinoid structures.

Figure 8 shows the IR transmission spectra of PPy films in each oxidation stage during the galvanostatic electrolysis of the PPy(TsO^-)/Ta electrode. The relatively strong band at 1547 cm^{-1} can be assigned to the conjugated double bond stretching vibration mode of the pyrrole ring.[17] A strong and sharp band at 1042 cm^{-1} is attributed to the **C-H** out of plane deformation of the quinoid form.[16] IR absorption bands attributed to TsO^- were observed at 1175(strong), 1117(weak), and 1087(medium) cm^{-1} in the Figure 8A.[18] As the galvanostatic electrolysis proceeded, the peak at 1547 cm^{-1}(C=C) of PPy (TsO^-) film increased and shifted slightly toward higher frequency. On the other hand, a new absorption peak assigned to the stretching vibration of a carbonyl (C=O) group, appeared at about 1700 cm^{-1} from the spectrum B. The carbonylation of PPy would arise from irreversible oxidation of pyrrole rings by **OH^-** attaching.[19] At the same time, the electrical conductivity of the PPy films during the electrolysis of the PPy(TsO^-) /Ta electrode decreased with the proceeding of the electrolysis(A: 106, B: 10, C: 7, and D; 5 Scm^{-1}). These indicate that the structure, in which the π-electron system of the polymer is partially interrupted,[20] proceeds with electrolysis.

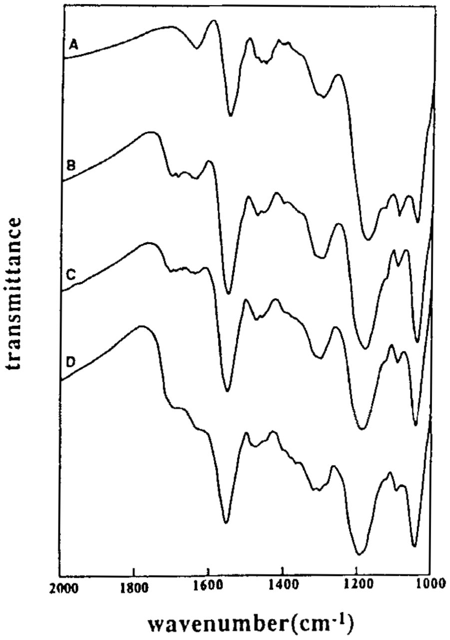

FIGURE 8. Infrared transmittance spectra of PPy(TsO^-) films. A, B, C, and D are correspond to the samples obtained from the conditions A, B, C, and D stages of Figure 7.(a).

ELECTRICAL CHARACTERISTICS OF PPy/Ta_2O_5/Ta SYSTEMS

A PPy/Ta_2O_5/Ta structure was investigated by making a simple Ta electrolytic capacitor as shown in Figure 9.

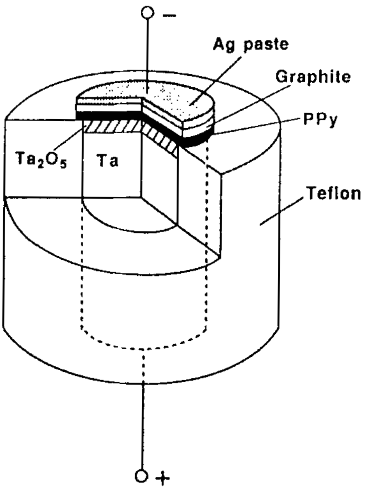

FIGURE 9. A model for the capacitor of prototype Ta solid electrolyte with a PPy film.

Table I shows the electrical characteristics of the three layer-structures (sample A and B) of PPy/Ta_2O_5/Ta. Sample A was prepared by simultaneous formation of PPy and Ta_2O_5 on a Ta electrode by the electropolymerization of pyrrole. Sample B was obtained from the galvanostatic electrolysis of the PPy/Ta formed previously by the electropolymerization. The electrical conductivity of PPy film of sample B was lower than that of the sample A. This is due to the irreversible oxidation of the PPy film at the electrolysis of the Ta electrode coated with PPy, accompanying the destroy of the conjugation of the polymer chains. The capacitance of sample B was larger than that of the sample A, corresponding to the thickness of Ta_2O_5 layers. The tan δ (dissipation factor) of sample A was low as 0.06, which was about 1/3 of sample B because the sample A is superior to sample B in the adhesion properties between the PPy films and Ta_2O_5 layers and the electrical conductivity. The leakage curfent(LC) were relatively small. This indicates that the insulating property of Ta_2O_5 was kept even after the electronic current through Ta_2O_5 at simultaneous formation of sample A.

TABLE I Electrical characteristics of resulting PPy/Ta_2O_5/Ta structure.

sample	σ(PPy) [S/cm]	D(Ta_2O_5) [nm]	capacitance (1V, 120Hz) [μF/cm^2]	efficiency (%)	tan δ (1V, 120Hz)	LC (5V, 30sec) [μA]
A	110	35	0.55	77	0.06	0.30
B	5	22	0.75	68	0.19	0.20

σ: electronic conductivity, D(Ta_2O_5): thickness of Ta_2O_5 layer,
efficiency: measured capacitance/calculated capacitance,
tan δ: dissipation factor, LC: leakage current.

The capacitance value of these prototype capacitors are significantly low because the surface area of the disk electrode is small. Sintered metal electrodes or etched metal electrodes are generally used as electrodes for capacitors. Though PPy is generally formed on the surface of the sintered-Ta electrode by usual electropolymerization methods, it was successfully prepared in the interior of the sintered electrode by us, recently. This would lead to the new method to prepare the PPy/Ta_2O_5/Ta structure in the sintered-Ta electrode by in-situ electropolymerization methods.

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