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Sintered-Tantalum Electrode Modified with Polypyrrole by Electropolymerization

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Synopsis. Polypyrrole (PPy) formation in the interior of a porous electrode by electropolymerization was considered to be impossible. When a concentrated pyrrole solution was soaked into a sintered-Ta electrode and electrolyzed in a pyrrole-free solution, PPy was formed in the interior. PPy occupied 70% of the inner space, and no defect was observed by SEM.

Electrically conducting polymers have been widely studied.[1] These days, investigations have focused on applications for electrical devices, such as batteries[2,3] and capacitors.[4,5] Particularly, polypyrrole (PPy) films having high electronic conductivity and stability have been extensively studied as electrolyte materials of solid electrolytic capacitors.

In order to apply PPy to capacitors, it is necessary to polymerize PPy electrically on such base metals as tantalum (Ta) or aluminum (Al). It was generally considered to be difficult to form PPy electrically on these metals, since they tend to form insulating oxide layers,[6] resulting in narrow potential windows. It is also necessary to obtain a large effective area of the insulating layer. Porous electrodes, such as etched-Al[4] or sintered-Ta, are generally used as the electrodes of commercially used capacitors. Though PPy in the interior of these electrodes is generally formed by chemical polymerization,[5] the conductivity of chemically polymerized PPy is low. Therefore, electropolymerization of pyrrole was attempted using chemically polymerized PPy as an electrode.[5] This method, however, requires many steps.

Recently, we succeeded to modify a Ta disk electrode, which had an insulting layer (Ta_2O_5) on its surface, with a PPy film by the electropolymerization of pyrrole.[7,8] However, it is also considered to be difficult to form PPy in the inner surface (interior) of a porous electrode, though the formation of PPy on the outer surface (apparent surface) of a porous electrode is easy. We studied the polymerization profiles of pyrrole in the interior of sintered-Ta electrodes, and report here on a soaking method which can easily form PPy in the interior of the electrode by electrolysis.

Experimental

Material. Two types of sintered-tantalum electrodes were used in the experiments. One was a large column type (5.03 mm ϕ, 7.15 mm H, effective surface area of 430 cm^2); the other was a small type (1 mm×2 mm×0.3 mm, effective surface area of 6.8 cm^2). They were made of Ta particles (1 µm ϕ).

Pyrrole (Tokyo Kasei Ltd.) was purified twice by distillation under a nitrogen atmosphere (58 °C, 56 mmHg, 1 mmHg=133.322 Pa) before electropolymerization. Propylene carbonate (PC; Kanto Chemical Co.) was purified by distillation under a nitrogen atmosphere (98 °C, 1.9 mmHg). Tetrabutylammonium perchlorate (TBAP: Tokyo Kasei Ltd.) was recrystallized from water/ethanol (2/3 vol/vol) and dried in vacuo for one day at 60 °C. A Britton–Robinson's buffer solution (pH=1.8) comprised phosphoric acid (0.04 M, M=mol dm^{-3}), acetic acid (0.04 M), and boric acid (0.04 M). Water was purified by a MILLI-Q Water Purification System (CDMB 012 02, CDFC 012 04, CP15 010 03, PMEG 090 02, MPGL 05C JJ).

Electropolymerization of Pyrrole. Electropolymerization of pyrrole was carried out using a sintered-Ta electrode as a working electrode, a stainless made cylindrical electrode (17 mm ϕ, 20 mm H) as a counter elelctrode, and a Ag/AgCl electrode (for organic solutions) or a saturated calomel electrode (SCE: for aqueous solutions) as a reference electrode. The potential was controlled by a dual potentiogalvanostat (Nikko Keisoku DPGS-1).

Conventional Method: Potentiostatic electrolysis (1.5, 5, and 10 V), or galvanostatic electrolysis (10 and 100 mA) was carried out in a pyrrole (0.1—10 M) solution containing a supporting electrolyte (0.1 M).

Soaking Method: At first, a concentrated pyrrole solution (0.75—14.4 M) containing a supporting electrolyte (0.01—0.5 M) was soaked into the sintered-Ta electrode. The electrode was then placed in a pyrrole-free electrolyte solution. Electrolysis was carried out potentiostatically (1.5, 5, and 10 V) or galvanostatically (1, 10, 100, and 1000 mA).

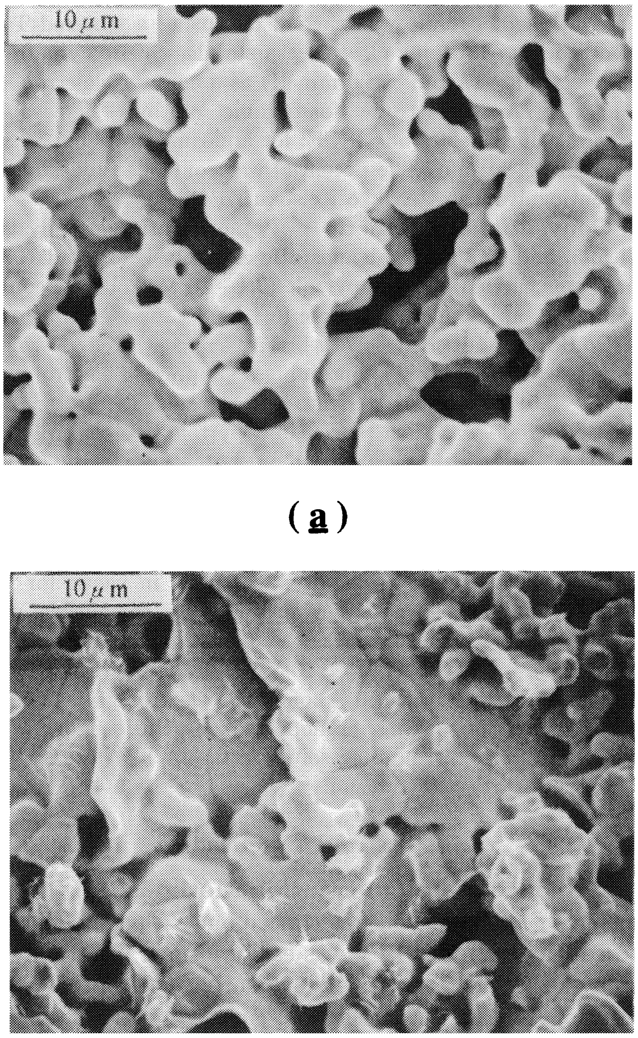
The weight of PPy formed in the interior of the electrode was measured after removing the PPy formed on the apparent surface of the electrode and drying in vacuo for 1 d at 40 °C. The formation rate of PPy on the surface of the electrode was measured in the conventional method (0.1 M-pyrrole, 0.1 M-TBAP/PC, 10 V potentiostatic electrolysis), and the rate in the interior of the electrode was measured using the soaking method (soaked solution: 0.1 M-TBAP/pyrrole, surrounding solution: 0.1 M-TBAP/PC, 10 V potentiostatic electrolysis).

Results and Discussion

Influence of Polymerization Methods. At first, a conventional method was carried out with a small sintered-Ta electrode. PPy was easily formed in the interior of the electrode involving methods used to form PPy on the Ta disk electrode;[8] electrolysis, however, needed a higher potential than those methods. Since a small electrode is very thin (0.3 mm), polymerization profiles in the interior of such an electrode would be almost the same as those on the surface. In cases involving a large electrode, the formation of PPy in the interior failed in all solution compositions and all conventional electrolysis, while PPy was formed sufficiently on the apparent surface of the electrode.

In a soaking method with over 5 V potentiostatic electrolysis, PPy was formed on the entire inner surface of the large electrode. Figure 1 shows SEM photographs of a fracture section of a sintered-Ta electrode. The naked Ta particles observed before electrolysis (a) were covered with PPy after electrolysis by the soaking method (b). No defect was observed by SEM. From the weight of PPy formed in the interior of the electrode, 70% of the inner space of the electrode was calculated to be occupied by the resulting PPy. This indicates that all of inner surface of the electrode was covered with the PPy film.

The difference in the formation of PPy between in the interior and on the apparent surface of the electrode should be due to the difference in the polymerization rates. The polymerization rate of pyrrole in unit molar concentration was 2.4×10^{1} [$\mathrm{mg\,min^{-1}\,cm^{-2}\,M^{-1}}$] in a conventional method. This value corresponds to the polymerization rate of pyrrole on the apparent surface of the electrode. The rate in the interior of the electrode, however, was 4.2×10^{-4} [$\mathrm{mg\,min^{-1}\,cm^{-2}\,M^{-1}}$] in the soaking method if the concentration of pyrrole in the interior was the same as that of the solution used for soaking. Such a five-order low polymerization rate in the interior of a sintered electrode proves the predominant formation of PPy on the apparent surface in conventional methods. In the case of the soaking method, the concentration of pyrrole in the interior was more than 10^{5}-fold higher than that of pyrrole in the surrounding solution (a small amount of pyrrole is leaked from the interior of the electrode). Then, the polymerization rate of pyrrole in the interior would exceed that on the apparent surface, resulting in the formation of PPy in the interior.



(b)

Fig. 1. SEM photographs of a fracture section of sintered-Ta electrodes (a: as received; b: after electrolysis by a soaking method).

However, only potentiostatic electrolysis produced PPy constantly within the entire interior of the electrode, even in the soaking method. This could be explained in terms of the difference in the breaking behavior of an insulating layer of the Ta electrode in a potentiostatic method[9] from that in a galvanostatic method. The surface of Ta metal is easily oxidized to form a thin oxide layer (as usual 20 Å thick[10]) in contact with oxygen in the air. In the case of a sintered electrode, it is impossible to remove the layer, for example, by polishing with abrasive paper. Therefore, the electrodes are used as received. Electropolymerization of pyrrole on the oxide layer is considered to be due to the leakage current, and a potential corresponding to the thickness of the oxide layer is necessary to breakdown the insulating layer.[7] The leakage current during galvanostatic electrolysis would flow more preferentially at the outer surface of the sintered electrode than at the inner surface, because the sintered electrode is surrounded by a cylindrical counter electrode. Once a part of an insulating layer facing the counter electrode has been broken, current would flow only at the broken point and form PPy on the outer surface of the electrode. The resulting PPy would block the holes of the electrode to shut the interior from the outside. That explains the reason that galvanostatic electrolysis failed to form PPy in the interior of the sintered electrode. In the case of potentiostatic electrolysis, the incline of the electrical potential in the oxide layer from the bulk electrode to the electrolyte solution should be the same in all surface of the electrode. Therefore, there are many chances for an electrical breakdown of the insulating layer, even on the inner surface of the electrode. A potentiostatic electrolysis at less than 1.5 V, which is sufficient for the electropolymerization of pyrrole on a polished Ta disk electrode, did not form PPy. This indicates the existence of a resistance of the insulating layer for breakdown.

Influence of the Kinds of Supporting Electrolytes and Solvents. A soaking method (soaked solution: 0.1 M electrolyte/pyrrole; surrounding solution: 0.1 M electrolyte/acetonitrile (AN), 10 V potentiostatic electrolysis) was used to determine the best electrolyte to form PPy in the interior. When TBAP was used, PPy was formed within the interior of the electrode. In the case of tetrabutylammonium tetrafluoroborate, PPy was formed in some parts of the interior. PPy was not formed at all when tetraethylammonium *p*-toluenesulfonate or *p*-toluenesulfonic acid was used.

A solvent effect was then studied with the soaking method (soaked solution: 0.1 M TBAP/pyrrole; surrounding solution: 0.1 M TBAP/solvents, 10 V potentiostatic electrolysis). In the case of AN, although PPy was formed in the interior, a soaked pyrrole solution leaked out from the sintered electrode because the density of pyrrole (0.97) was higher than that of AN (0.78). This prevents the sufficient amounts of PPy formation in the interior. The dendrite formation of PPy from the apparent surface of the electrode was serious in the case of AN and DMF, while a good and smooth PPy film was obtained in the case of PC. When an aqueous solution (e.g., a Britton–Robinson's buffer solution) was used as a surrounding solution, a phase separation between the surrounding solution and the soaked pyrrole solution was observed because of the poor solubility of pyrrole in water, and PPy was not formed in the interior. Therefore, PC was evaluated to be the best solvent.

Influence of Composition of Soaked Solutions. Figure 2 shows the influence of the pyrrole concentration of a soaked PC solution containing 0.1 M TBAP on the formation of PPy in the interior of a sintered-Ta electrode (surrounding solution: 0.1 M TBAP/PC, 10V potentiostatic electrolysis). The weight of PPy formed in the interior of the electrode increased with the pyrrole concentration. When the pyrrole concentration was above 75 vol%, the weight of PPy decreased. At a low pyrrole concentration, the formation rate of PPy was proportional to the pyrrole concentration. However, a decrease in the amount of formed PPy at high pyrrole concentrations of more than 75 vol% would be due to the low degree of dissociation of the electrolyte (TBAP). As shown in Fig. 2, the ionic conductivity of the soaked solutions gradually increased with the pyrrole concentration up to 50 vol%, and then decreased abruptly. Dissociation of TBAP would be promoted by an increase in the donor number of the solution with the pyrrole concentration. At higher pyrrole concentrations, dissociation would be restrained by the lower dielectric constant of the solution. Therefore, the pyrrole concentration of 75 vol% was determined to be the best pyrrole concentration as a soaked solution. That was supported by studying the effect of the concentration of TBAP in pyrrole as soaked solutions. The amount of the formed PPy increased linearly with the TBAP concentration. This could also be explained in terms of an increase in the ionic conductivity of the solution, namely an increase in the number of electrolyte ions.

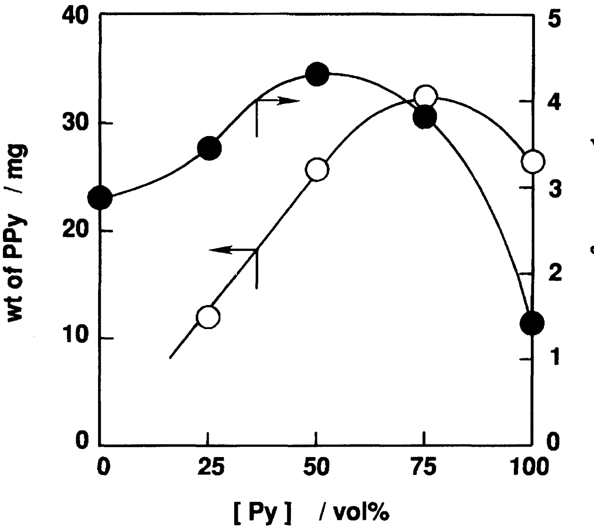


Fig. 2. Influence of the pyrrole concentration of soaked solutions on the weight of PPy (○) and the solution conductivity (●). (soaked solutions: 0.1 M TBAP/(pyrrole+PC); surrounding solution: 0.1 M TBAP/PC; 10 V potentiostatic electrolysis, 600 s).

In conclusion, the formation of PPy in the interior of a sintered-Ta electrode was successful due to the development of a soaking method. This technique should lead to a simple preparation of a PPy solid electrolytic Ta-capacitor by electrolysis The details concerning the electrical properties of the capacitor will be reported in the near future.

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