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Electrochemical properties of carbon xerogels coated with poly(p-fluorophenylthiophene)

J. Yamashita[a,*], M. Shioya[b], Y. Soneda[a], M. Kodama[a], H. Hatori[a]
[a]*National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan*
[b]*Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan*

Electroconducting polymers have attracted considerable attention as electrode materials for electrochemical capacitors because of their large charge storage capacity [1]. The rate performance of electroconducting polymers, however, is inferior to that of electric double-layer capacitors. This is because the charge storage in electroconducting polymers is based on the electrochemical doping in which the counter ions are inserted in the polymer matrix for maintaining the electronic neutrality. In order to improve the rate performance, it is necessary to enlarge the surface area of electroconducting polymers by depositing them on a porous substrate. In the present study, the electrodes consisting of poly(p-fluorophenylthiophene) (PFPT) and carbon xerogel (CXG) was fabricated using electrochemical polymerization. Since PFPT has the ability to dope cations and anions, it is applicable to the electrodes for type-III capacitors [1]. CXGs have suitable properties for polymerization electrodes such as high porosity, electric conductivity and corrosion resistivity [2]. In the present study, first of all, the relation between electrochemical properties and thickness of PFPT layer was investigated for the PFPT layer formed on a non-porous carbon film with the aim of determining the optimum layer thickness. Then, CXGs coated with PFPT layer having an appropriate thickness were prepared and their electrochemical properties were characterized.

The dedoping capacity obtained by cyclicvoltammetry at various sweep rate are shown in Fig. 1 as a function of polymerization charge density (Q_{poly}). The change of capacity with Q_{poly} and its dependence on sweep rate are different between Q_{poly} below and above 0.01 mAh cm^{-2}. Above 0.01 mAh cm^{-2}, the capacity is decreased with increasing Q_{poly} and the decrease is made larger with increasing sweep rate. This is caused due to the insufficiently slow diffusion of ions in the polymer matrix. The change of capacity with Q_{poly} below 0.01 mAh cm^{-2}, however, can not be interpreted in terms of the diffusivity of ions.

Fig. 2 shows the relation between stoichiometric number (N) for electrochemical polymerization of FPT and Q_{poly}. The value of N corresponding to the ideal polymerization is 2 [3]. The value of N is significantly larger than 2 at Q_{poly} below 0.01 mAh cm^{-2}. This indicates that some side reaction take place preferentially. It is considered, therefore, that the small capacity at Q_{poly} below 0.01 mAh cm^{-2} results from the existence of structural defects in PFPT molecules. From the results shown above, it is concluded that the layer thickness of about 200 nm which is attained by polymerization giving Q_{poly} of 0.01 mAh cm^{-2} is the optimum one for maximizing the capacity.

The pores in CXGs used as the substrate must be so large as not to lose the contact with external surface even when PFPT coating is applied. In the present study, CXGs with average pore diameter of about 450 nm were prepared according to the procedure proposed by Saliger [2].

When the PFPT coating of CXGs was conducted by electrolyzing the monomer solution similarly to the case of carbon films, PFPT was deposited only on the external surface of CXG. In order to overcome this problem, monomer was first impregnated into CXG and then it was polymerized in the monomer-free electrolyte. Consequently, CXG could be coated homogeneously with PFPT layer having the thickness of about 100 nm.

The cyclicvoltammograms for PFPT-coated CXGs are shown in Fig. 3. At sweep rate of 1 mV sec^{-1}, PFPT-coated CXG shows the capacity comparable with that for PFPT layer with optimum thickness. The capacity, however, is significantly reduced by increasing the sweep rate up to 100 mV sec^{-1}. This is because the resistance of electrode is not negligibly small. In order to decrease the resistance of electrode, the present authors are improving the geometry of CXG and the contact between CXG and current collector.

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[2] Saliger R, Bock V, Petricevic R, Tillotson T, Geis S, Fricke J. J Non-Cryst Solids 1997;221(2-3):144-150.
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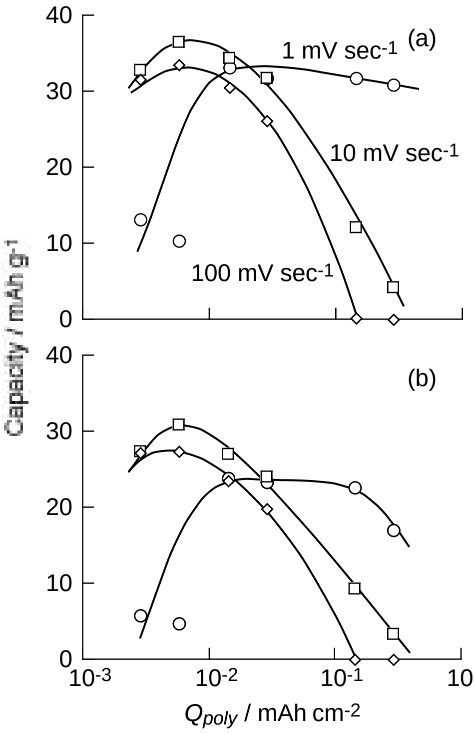

Fig. 1 Capacity in first (a) p- and (b) n-dedoping processes versus polymerization charge density (Q_{poly}) for PFPT layer formed on non-porous carbon film. Sweep rate of cyclicvoltammetry are shown in the figure.

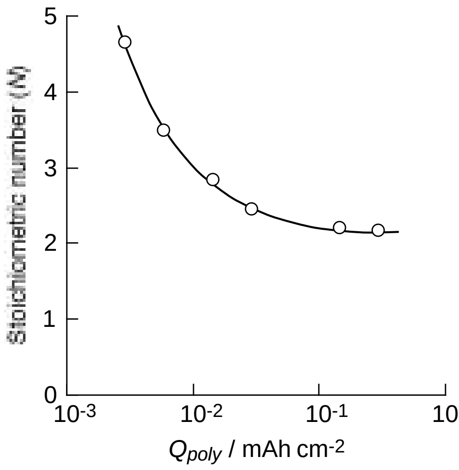

Fig. 2 Stoichiometric number for electrochemical polymerization of FPT (N) versus Q_{poly}.

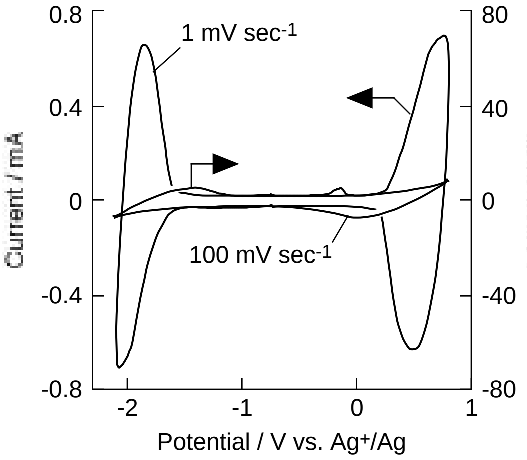

Fig. 3 Cyclicvoltammograms for PFPT-coated carbon xerogels. Sweep rate are shown in the figure.