Preparation of carbon xerogels coated with poly(p-fluorophenylthiophene) and their properties for electrochemical capacitor

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1. Introduction

Electroconducting polymers have attracted considerable attention as electrode materials for electrochemical capacitors [1,2]. Compared with electric-double layer capacitors, the conducting polymers show larger charge storage capacity while their rate performance is inferior. This is because the charge storage in the conducting polymers is based on elctrochemical doping in which ionic species are inserted in polymer matrix for maintaining the electronic neutrality. In order to improve the rate performance, it is necessary to enlarge the surface area of conducting polymers by developing the porous structure. It is quite difficult, however, to process the conducting polymers into a desired shape by applying an additional treatment because of the lack of solubility and fusibility. Therefore, the processing of the conducting polymers has to be made simultaneously with polymerization.

Polymerization techniques for the conducting polymers are classified into chemical and electrochemical ones. The electrochemical polymerization allows the conducting polymers to form the layer on the electrode. The layer thickness can be controlled over a wide range by changing the electrolysis conditions. If the polymer layer is formed on the porous electrode in an appropriate thickness, the conducting polymer electrode with high porosity will be obtained.

In the present study, an attempt was made to fabricate the electrode consisting of poly(p-fluorophenylthiophene) (PFPT) and carbon xerogel. Since PFPT shows a large capacity in p- and n-doping processes and a large potential difference between these processes, it is applicable to anode and

cathode in capacitors [1-3]. Carbon xerogels have suitable properties for the polymerization electrodes such as high electric conductivity, porosity and corrosion resistivity, which are derived through sol-gel polycondensation, subcritical drying and high temperature heat-treatment [4]. In the present study, first of all, the relation between electrochemical properties and layer thickness was investigated on the PFPT layer formed on the non-porous carbon film with the aim of determining the optimal layer thickness. Then, the carbon xerogels was coated with the PFPT layer having an appropriate thickness, and the electrochemical properties of the resulting electrodes were characterized.

2. Experimental

p-Fluorophenyl thiophene (FPT) monomer was synthesized by nickel(II)-catalyzed coupling reaction according to the literature [5,6] and purified by sublimation under a reduced pressure. Propylene carbonate (PC) and PC solution of 1 M tetraethylammonium tetrafluoroborate (Et$_4$NBF$_4$) (Tomiyama Pure Chemical Industries, Ltd.) were used as received. Non-porous carbon films with thickness of 100 μm were obtained by heating polyimide films (UPILEX, UBE Industries, Ltd.) up to 1500°C under nitrogen gas flow. Carbon xerogels were prepared from aqueous solution of resolcinol, formaldehyde and sodium carbonate using the procedure described in the literature [4]. The mass fraction of resolcinol and formaldehyde in the solution was adjusted to be 0.3. The molar ratios of formaldehyde and sodium carbonate against resorcinol were 2 and 1/1500, respectively. The solution was gelated by two-step heat-treatment at 20 and 50°C for 7 and 4 days, respectively. In order to prevent a large shrinkage during drying, water in the wet gel was firstly exchanged with acetone and then acetone was removed from the gel by evaporation. The organic xerogels were carbonized by heating them up to 1500°C under nitrogen gas flow.

All electrochemical experiments were performed using a three-electrode cell connected to a computer-controlled multi-potentiostat system (VMP, Bio-Logic SA). The cell was partitioned into three compartments for working, counter and reference electrodes by a porous glass frit. The counter electrode was a platinum foil with the sizes of 1.0 cm by 1.5 cm (surface area=3.0 cm^2). Two different working electrodes were fabricated using the carbon films and carbon xerogels as follows: In the case of carbon films, the specimen with a spade shape was served as the working electrode. The head of specimen had the sizes of 1.1 cm by 1.6 cm (surface area=3.5 cm^2). The neck of specimen was isolated from the electrolyte by epoxy resin coating. For the carbon xerogels, the working electrode was prepared by binding the rod-

like specimen and platinum wire with Teflon tube which was radially shrank by heating. The diameter and length of specimen were 0.2 and 1.0 cm, respectively. The reference electrode was a silver wire immersed in the the acetonitrile solution containing 0.1 M tetrabutyammonium perchlorate and 0.01 M silver nitrate. The calibration of reference electrode was made by performing cyclicvoltammetry with a platinum foil immersed in PC solution containing 1 M Et_4NBF_4 and 5 mM ferrocene at a sweep rate of 10 mV sec^{-1}. The half-potential of ferrocenium/ferrocene redox couple was measured to be 0.07 V with respect to the reference electrode. This was almost consistent with the result shown in the literature [6]. In this paper, the potential will be represented as the value with respect to the reference electrode.

Electrochemical polymerization of FPT on the carbon electrodes was carried out using two different techniques as follows: In the case of carbon films, FPT dissolved in electrolyte was electrolyzed at a constant potential. The compartment for working electrode was filled with the PC solution of 0.5 M Et_4NBF_4 containing 0.1 M FPT, while that for the counter electrode was filled with the monomer-free electrolyte. FPT was polymerized on the carbon film by electrolysis at the constant potential of 1.05 V until the desired amount of charge was passed. Then, the resulting PFPT layer was neutralized by sweeping the potential to 0 V at the rate of 1 mV sec^{-1} and held at this potential until the current was decreased to 1 μA. The electrode was taken out of the cell, washed with tetrahydrofuran and dried under a reduced pressure at room temperature. The mass of PFPT layer on the carbon film was measured to an accuracy of 1 mg in air. In the case of carbon xerogels, FPT which was preliminary impregnated in the specimen was electrolyzed at a constant potential in the monomer-free electrolyte. The PC solution saturated with FPT was first impregnated into the electrode under a reduced pressure. Then, the electrode was placed in the PC solution of 0.5 M Et_4NBF_4 and the constant potential of 1.05 V was applied. The current was decreased with the progress of polymerization due to the reduction of residual monomer. After the current reached 1 μA, the PFPT film was neutralized as described above.

Electorchemical properties of PFPT-coated carbon electrodes were characterized by cyclicvoltammetry. The compartments for both working and counter electrodes were filled with PC solution of 1 M Et_4NBF_4. For the PFPT-coated carbon xerogels, the electrolyte was impregnated into the specimen under a reduced pressure prior to the cell assembly. The range of potential sweep was determined to be -2.1-0.8 V by taking into account the potential window of electrolyte. The rate of potential sweep was varied in the range of 1-100 mV sec^{-1}. All electrochemical experiments were conducted in a glove box under a pure argon at room temperature.

3. Results and discussion

By using electrochemical polymerization, the PFPT layer with an uniform thickness was formed on the carbon film. The thickness of PFPT layer was increased in proportion to the polymerization charge per unit surface area (Q_{poly}) and reached about 8 μm at Q_{poly} of 0.28 mAh cm^{-2}. In the cyclicvoltammogram of PFPT layer, two peak couples which were assigned to p- and n-doping/undoping appeared at the potential ranges of 0.2-0.8 V and -2.1--1.6 V, respectively. The values of charge passed at these potential ranges were defined as p- (Q_p) and n-doping capacity (Q_n), respectively. The capacitance in p- (C_p) and n-doping (C_n) were obtained by dividing Q_p and Q_n with the potential difference of 0.6 and 0.5 V, respectively. The capacity and capacitance at various sweep rate are shown in Fig. 1 as a function of Q_{poly}. In both p- and n-doping, the maximum capacitance exceeds 210 F g^{-1}. 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 because the ionic species can not be inserted in the internal portion of PFPT layer due to the insufficiently slow diffusion of ionic species in the polymer matrix. On the other hand, below 0.01 mAh cm^{-2}, the thickness of PFPT layer is so small that the ionic species can be inserted over the whole layer even under fast potential sweep. Thus, the capacity is determined due to the structural feature of PFPT layer. The change of capacity with Q_{poly} suggests that there is a structural difference between PFPT layers with different thickness.

In order to investigate the change of reaction mechanism during polymerization, the stoichiometric number (N) was calculated as follows

$$N=(Q_{poly}-Q_{neu})M_n/(Fm) \tag{1}$$

where M_n is the molecular weight of FPT, Q_{neu} the neutralization charge, F Faraday constant, and m the mass of PFPT. The value of N corresponding to the ideal polymerization reaction of FPT is 2 [7]. As shown in Fig. 2, the value of N is considerably 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 introduced by side reaction. From the results shown above, it is concluded that the layer thickness of about 200 nm which is
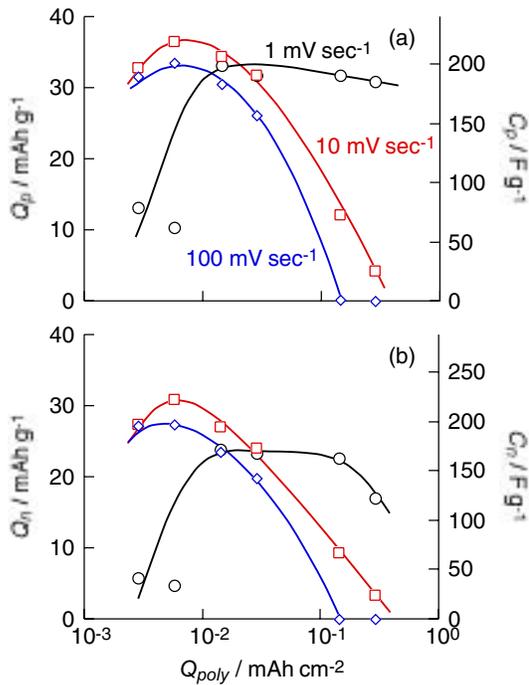
Fig. 1   Capacity and capacitance for first (a) p-
(Q_p and C_p) and (b) n-undoping processes (Q_n
and C_n) versus polymerization charge density
(Q_{poly}) for poly(p-fluorophenyl thiophene) layer
formed on non-porous carbon film. Sweep rate
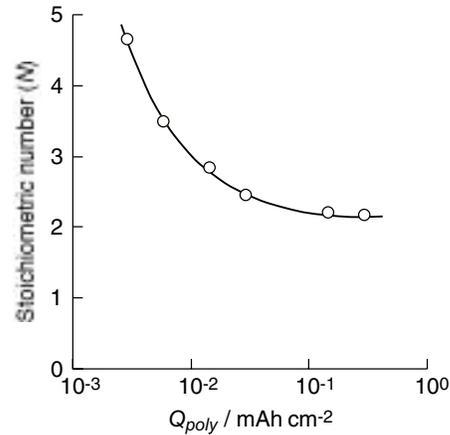of cyclic voltammetry are shown in the figure.

Fig. 2   Stoichiometric   number   for
electrochemical   polymerization   of   p-
fluorophenylthiophene (N) versus polymerization
charge density (Q_{poly}).

achieved by polymerization giving Q_{poly} of 0.01 mAh cm^{-2} is optimal one from
the view point of maximizing the capacity.

The pores in carbon xerogels used as the substrate have to be so
large as not to lose the contact with external surface even when PFPT coating
is applied. In the present study, the carbon xerogels with average pore
diameter of about 450 nm were prepared according to the procedure
proposed by Saliger [4].

When the PFPT coating on carbon xerogel was performed similarly to
the carbon film, PFPT was deposited only on the external surface of the
specimen. In order to overcome this problem, FPT which was preliminary
impregnated in the carbon xerogel was elctrolyzed in the monomer-free
electrolyte. As a result, the carbon xerogel could be coated homogeneously
with PFPT layer having the thickness of about 100 nm.

The cyclicvoltammograms for the carbon xerogels before and after applying PFPT coating are compared in Fig. 3. At sweep rate of 1 mV sec^{-1}, the capacitance arising from the doping of PFPT is close to the value calculated from the result for the PFPT layer formed on the carbon film. The doping capacitance, however, is significantly reduced with increasing sweep rate up to 100 mV sec^{-1}. Considering the thickness of PFPT layer as small as 100 nm, this result can not be explained in terms of the diffusivity of ionic species.
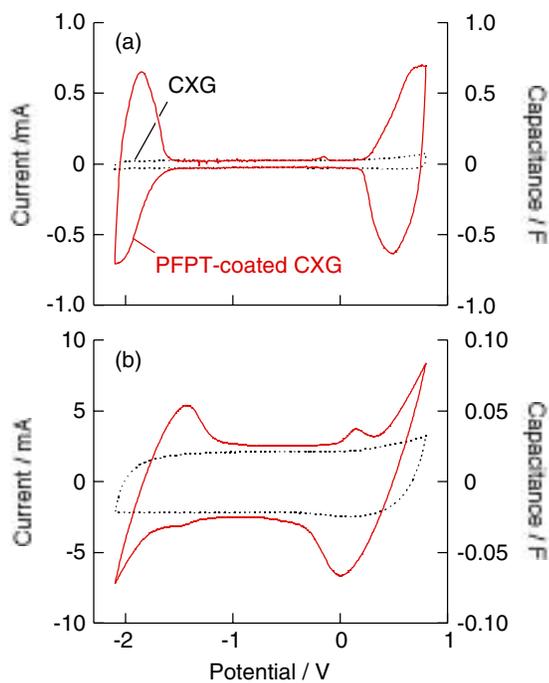

Fig. 3 Cyclicvoltammograms for carbon xerogel and PFPT-coated carbon xerogel at sweep rates of (a) 1 and (b) 100 mV sec^{-1}.

In the PFPT-coated carbon xerogel, the carbon xerogel functions as

an electric path between PFPT layer and current collector. If the resistance of carbon xerogel and current collector including the contact resistance between these materials is not negligibly small, the effective potential applied to PFPT layer is decreased. This results in the reduction of doping capacity. The resistance of carbon xerogel electrode prepared in the present study was not small because of a large size of carbon xerogel and small contacting area between carbon xerogel and platinum wire. This is the cause for the reduction of doping capacity with increasing sweep rate. In order to decrease the resistance of electrode, the present authors are improving the geometry of carbon xerogel and the contact between carbon xerogel and current collector.

4. Summary

For the PFPT layer formed on the carbon film, the dependence of capacity on layer thickness was investigated. The layer thickness of about 200 nm which was achieved by polymerization giving Q_{poly} of 0.01 mAh cm^{-2} was optimal one for maximizing the capacity. The carbon xerogels with porous structure suitable for applying PFPT coating were prepared. By using the polymerization technique consisting of the impregnation of monomer solution followed by the electrolysis in monomer-free electrolyte, it was possible to coat the carbon xerogel homogeneously with PFPT layer. The PFPT-coated carbon xerogels showed a large capacity close to the value expected from the rule of mixtures under slow potential sweep. Only a fraction of expected capacity, however, could be obtained under fast potential sweep due to the large resistance of electrode.

Acknowledgements

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