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STRUCTURE AND EDLC APPLICATIONS OF PVDC BASED CARBONS AS A FUNCTION OF CARBONIZATION TIME

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Poly-vinylidenechloride (PVDC) based carbon has been used as an electrode material for electric double layer capacitor (EDLC) due to novel characteristics, which inherited from the pristine PVDC. Electrochemical and morphological properties of three PVDC based carbon with different retention time from 60 min to 180 min were characterized by a conventional gas adsorption method and the image analysis using transmittance electron microscopy (TEM).

Keywords: PVDC based carbon material; duration time; double-layer capacitance; image analysis

INTRODUCTION

Among carbon materials, poly vinylidene chloride (PVDC) based carbon has a novel property that makes it attractive for use as a carbon precursor material. Researchers have investigated various properties of PVDC [1–3]. In this work we apply this material to the electrochemical applications field as high-power capacitance devices. We have previously reported that PVDC-based carbon is a suitable electrode material for the polarizable electrode of a double layer capacitor [4]. This material has excellent advantage for use as an electrode material for electric double layer capacitor because of the following considerations: 1) No additional activation process is required, this being the most expensive cost in the

manufacturing process for obtaining a porous structure and, besides, 2) the specific capacitance obtained with of this precursor material is considerably higher than that obtained with other materials reported up to now. The specific capacitance was found to reach over 100 F/g (which is equivalent to 400 F/g for a single electrode). In this study, retention time dependence of double layer capacitance was investigated. Furthermore, the new model based real observation for the description of double layer capacitance was suggested.

EXPERIMENTAL

Homogeneous PVDC with the crystallite size of 267 Å was chosen as a pristine material for preparing an electrode for an EDLC. Sample was heat-treated in an inert atmosphere of N_2 using various holding times in the range from 60 to 180 minutes at a constant heat treatment temperature (HTT) of 700°C. After the grounding, coin type electrode was made with 5 wt%, polytetrafluoroethylene (PTFE) as a binder. Electrode dimension is 13.45 mm in diameter and 0.4 mm in thickness. Capacitance measured using a unit cell system (a two electrode system) [5] with constant current. Charging was performed with current at 5 mA, and discharges were performed at various current densities, with a 30 wt% sulfuric acid aqueous solution. Platinum plate was used as a collecting electrode. Glass paper (Oribest) was used as a separator that is around 180 μm in thickness. Charge voltage was limited at 0.9 V to prevent the decomposition of water. The following measurements were performed to characterize the structure of the PVDC-based carbon: specific surface area measurements (SSA, Gemini 2375, SHIMADZU, Co., Japan), field emission transmission electron microscopy (FE-TEM, JEOL JEM-2010FEF, accelerating voltage 200 kV), and image analysis for the pore size distribution (PSD) of the samples.

RESULTS AND DISCUSSION

The N_2 adsorption isotherms of PVDC-based carbon heat-treated from 60 to 180 min at 700°C are performed. The adsorption of N_2 was almost completed at a low relative pressure, under $P/P_0 = 0.1$ in all samples. That is, all isotherms shows type I behavior, implying a microporous structure. The specific surface area (SSA) decreases with increasing the retention time for heat treatment (Fig. 3). However, the range shows a more drastic decrement of SSA in the range between 60 and 120 min than that in the range between 120 and 180 min. Figure 1 shows the pore size distributions (PSDs) that were calculated from the adsorption isotherms using MP methods [6]. However, it is hard to distinguish the difference of pore size

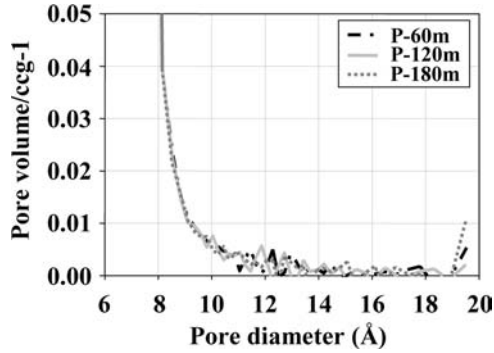

FIGURE 1 Pore size distribution (PSDs) of PVDC-bassed carbon samples heat-treated from 60 to 180 min at 700°C.

distributions of samples by conventional gas adsorption. Figure 2 shows that the specific capacitance per weight (a) and volume (b) as a function of current density. Amazingly, all of the capacitance values obtained from this experimental data exceed 85 F/g at 1 mA/cm^2 discharge current density. Especially, for the case of P-120 m, Figure 2(a) shows a capacitance as high as 100.2 F/g, which is equivalent to 400.8 F/g in a conventional three-electrode system. This is the largest value for a static double layer capacitor with no Faradaic reaction that has been reported up to now, except the electrochemical capacitors accompanied by Faradaic reactions [5].

Figure 3 shows the variation for specific capacitance (F/g) and the specific capacitance as a function of the retention time. Figure 3 clearly shows that the specific capacitance is not proportional to the SSA. That is, it should be considered in the other point of view. Figures 4(a),(b),(c) show the original TEM images (α), the corresponding power spectra obtained by

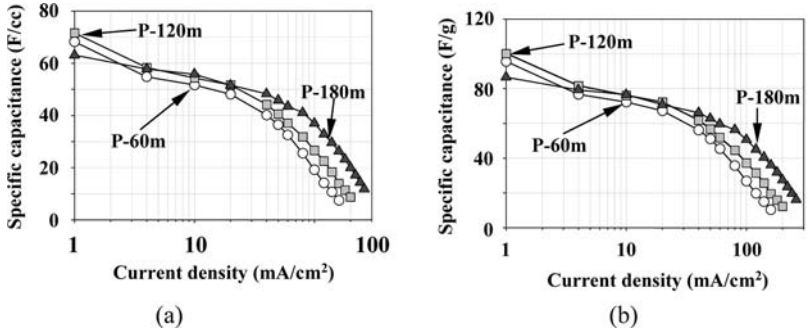

FIGURE 2 Specific capacitance profiles for 3 samples per weight (a) and volume (b) for the 3 samples with different retention times for heat treatment.

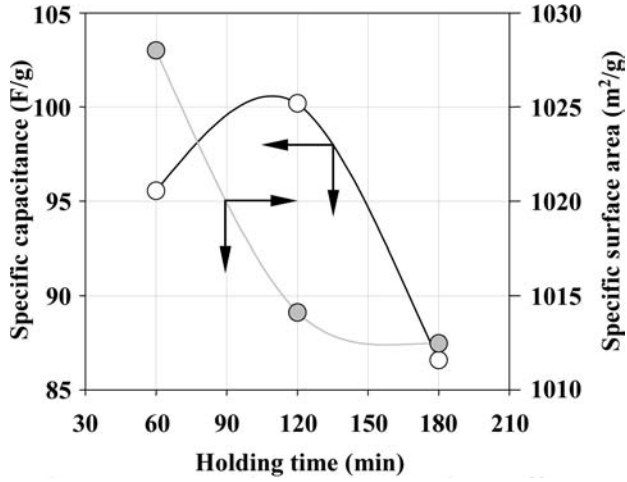

FIGURE 3 Retention (holding) time effect of the heat-treatment on the specific capacitance and on the specific surface area.

taking the two-dimensional FFT (fast Fourier transform) (β), and the pore size distributions of the TEM images analysis (γ). In contrast to the SSA results, which obtained by the conventional nitrogen adsorption method, it shows no conspicuous difference. However, the novel method using analysis of the TEM image shows a clear difference in their pore size distributions (PSDs). As the retention time increases, the contribution of the large pores to the PSD increases. That is, for the sample P-60 m (Fig. 4(a)), the pore size around 12 Å is the predominant while the other sizes of pore faction are relatively small. Such a concentration on distribution for P-60 m is attributed to the puffing phenomenon by the chlorine and/or HCl gas, which were contained in the pristine PVDC. For the P-120 min (Fig. 4(b)), maximum peak in pore diameter shift to around 9 Å, which is the most proper size for aqueous sulfuric acid electrolyte [4]. The contraction of pore diameter is attributed to the condensation reaction by the heat treatment. However, pores exist in the PVDC based carbon material are collapsed and broaden by the coalescence of pore. Coalescence of pore structure has develops to the larger pore size. For P-180 m (Fig. 4(c)), it was confined that the development of pore size and the occurrence of new pore fraction.

CONCLUSIONS

The subtle pore size variation of PVDC-based carbon was possible to be quantified by the image analysis with TEM, while the conventional gas

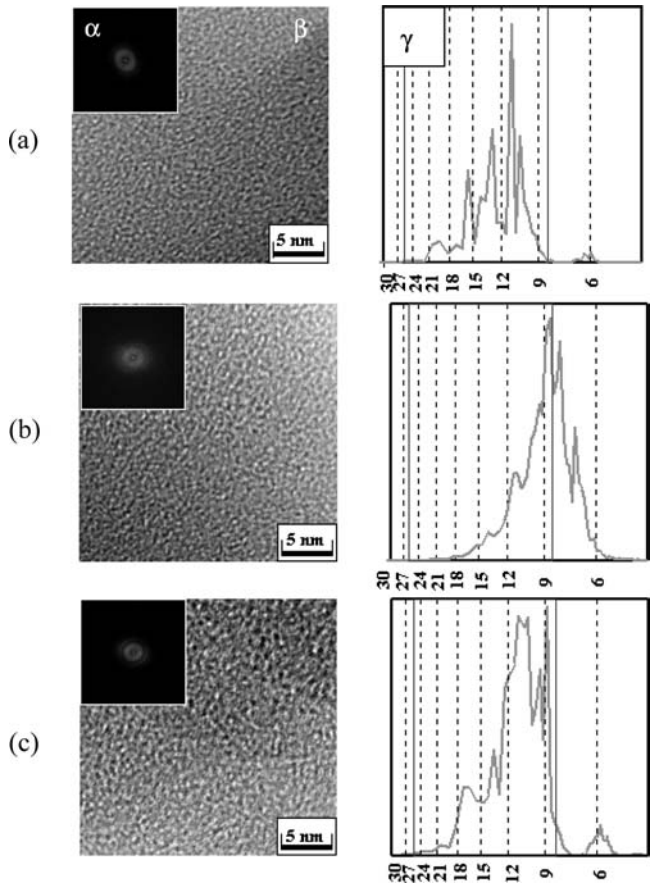

FIGURE 4 TEM photographs of (a), (b), (c) the sample with different retention time at 700°C. It was treated for 60 min ((a), P-60 m), 120 min ((b), P-120 m) and 180 min ((c), P-180 m). The results include the power spectrum obtained from a two-dimensional FFT (fast Fourier transform) (α), the original TEM image (β) and the pore size distribution obtained form TEM images analysis (γ).

adsorption method is hard to distinguish the pore size distribution among them. Especially, PVdC based carbon treated 120 min at 700°C shows a larger specific capacitance than any other materials, which has been reported up to now, as high as 100.2 F/g in a two-electrode system, it is equivalent to 400.8 F/g in a conventional system with reference electrode. It was confirmed that the variation of the pore size obtained by the heat treatment duration would greatly affect the capacitance performance.

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