

# Correlation between the pore and solvated ion size on capacitance uptake of PVDC-based Carbons

Kim YJ<sup>1</sup>, Horie Y<sup>1</sup>, Ozaki S<sup>1</sup>, Matsuzawa Y<sup>1</sup>, Suezaki H<sup>1</sup>, Endo M<sup>1</sup>  
<sup>1</sup>Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano,  
380-8553, Japan

*Corresponding author e-mail address: endo@endomoribu.shinshu-u.ac.jp*

## Introduction

Among the high porous carbon candidate for an electrochemical double-layer capacitor, *poly*(vinylidene chloride) (PVDC)-based carbon shows attractive characteristics with respect to cost, specific capacitance and ease of production [1]. This material can have a sufficient level of porosity to be of practical interest by applying a heat-treatment step without any additional activation, which would lead to greater expense. However, the capacitor properties were investigated in a previous report, which restricted the application to an aqueous electrolyte system [1]. The use of nonaqueous electrolyte for electrochemical capacitors is preferred since higher operating voltages (V) can be obtained due to the larger decomposition limits of the electrolyte solution. Furthermore, we considered the mechanism of pore formation on the basis of thermal behavior. The key mechanism in porosity formation by KOH etching is presumed to be associated with carbon oxidation. Carbon etching with KOH has been reported to be more effective for porosity development than etching via physical methods. This study is devoted to the application of carbons, derived from PVDC, for nonaqueous electrodes in EDLCs.

## Experimental

The starting material for the electrodes is homogeneous *poly*(vinylidene chloride) (PVDC,  $-\text{CH}_2\text{CCl}_2-$ , Asahi kasei Co.). It was calcined at 400°C under an inert nitrogen ( $\text{N}_2$ ) atmosphere and subsequently heat-treated at a final temperature. The samples prepared under these conditions are named from here on as 400-AVDC (*i.e.* 400°C-annealed PVDC based carbon under a nitrogen flow). The samples were prepared only by heat treatment at temperatures in the range of 600 - 1000°C in an  $\text{N}_2$  atmosphere, which were

designated the Npv-series. Another series of samples, the Apv-series, were activated by 400-AVDC and then chemically treated with a fixed KOH fraction of 200wt. % to 400-AVDC (reagent grade, Junsei chemical Co. Ltd., Japan). The activation was carried out under a fixed nitrogen flow and a predetermined residence time (1 h). The sample was then cooled by the nitrogen flow and washed with distilled water, which was obtained by purification and deionization (Iuchi, IP-315N2, Japan) to eliminate any residual contaminant. Finally the samples were dried at 110°C.

## Results and Discussion

Figure 1 shows the results of the thermo-gravimetric analysis (TGA; DTG-60, TA-60WS, Shimadzu, Japan) for pristine *poly*(vinylidene chloride) (PVDC), 400°C-annealed PVDC(400-AVDC) and its mixture with the KOH(200wt.%). All experiments were carried out under an inert atmosphere. The PVDC sample annealed at 400°C under an inert atmosphere shows a different thermal behavior than that of pristine PVDC. The weight variation *ca.* 200°C, due to decomposition of chlorine atoms, disappeared after the annealing at 400°C. However, a broad variation near 500-600°C was still observed, thus confirming its relation with the continuous structural coalescence of PVDC-based carbon as a function of HTT. The addition of KOH also affects the thermal behavior, which shows a drastic variation *ca.* 100°C. This decrease might be originated from the moisture in the KOH.

Figure 2 shows the yield variation of the Npv- and the Apv-series as a function of HTT. The values presented in here were calculated from the weight of pre-heat treated PVDC-based carbon at 400°C(400-AVDC). Heating rate was fixed at 5°C/min and heat treatment was maintained for 1 h at a target temperature. All values were calculated from the 400-AVDC, which has 34.6 wt. % from the pristine PVDC. It was confirmed that there were some deviation expected from the least square method, which is considered as an error originated from the small amount of the samples. However, the general tendency of yield variation could confirm, that is, residual weight amount by heat treatment decrease as the HTT increase. Furthermore, Npv-series has the yields around 2 times compared with those of the Apv (200)-series and the yield decrement of the Apv(200)-series is more drastic than those of the Npv-series. Figure 3 (a) and (b) show comparisons of the specific capacitance of both series of PVDC-based carbons using the constant-current method of a two-electrode

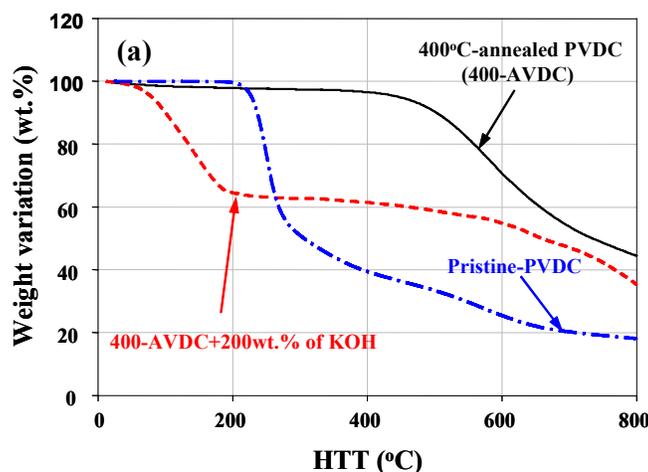


Figure. 1 TGA profiles as a function of HTT, obtained from 400 °C annealed PVDC (400-AVDC) based carbon, previous to heat treatment at the final temperature and its mixture with KOH (200wt. %).

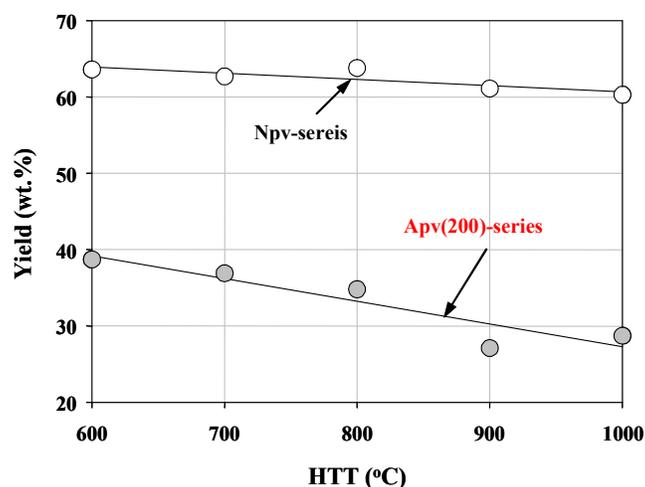


Figure. 2 Yield variations of the Npv- and the Apv-series as a function of HTT.

system. The capacitance per unit weight (a) and per unit volume (b) are presented here as a function of heat treatment temperature (HTT). From the results, the capacitance difference between the two series of PVDC-based carbons is clarified in a nonaqueous electrolyte. Although the Npv-series shows an excellent specific capacitance over a 100 F/g (equivalent to 400F/g for the conventional three-electrode system, see ref. 24 where the difference between 3 and 2 compartment systems are explained in detail) in aqueous sulfuric acid in previous report [8], it shows a small value in a nonaqueous electrolyte system. The variation of the capacitance shows the greatest deviation for the HTT 900

sample. Heat treatment at 900 °C is the most effective temperature for the Et<sub>4</sub>NB<sub>4</sub>/PC system, and Fig. 3(a) shows that a specific capacitance of 38.5 F/g was obtained for heat treatment at 900 °C, which is equivalent to 154 F/g when it is converted to the conventional three-electrode system method. Considering the capacitance by a volume fraction, there is a slightly different tendency. The specific capacitance of the Apv-series per unit volume has a maximum at HTT 800 and then it decrease again. However, as for the Npv-series no anomalous results are observed. By applying the KOH activation, extremely high capacitance could obtain as high as 8 times on the basis of weight and 6 times on the basis of volume compared with those of Npv-series in non-aqueous electrolyte system.

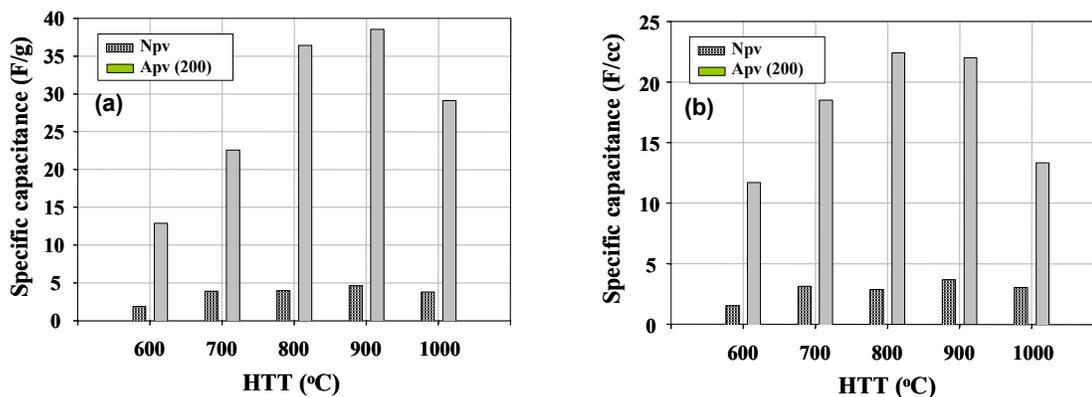


Figure. 3 Effect of KOH addition (200wt. %) on the specific capacitance per unit weight (F/g) (a) and the unit volume (b) of PVDC-based carbons. The dependence of the HTT is also present.

## Conclusions

PVDC-based carbon as a nonaqueous EDLC electrode was firstly investigated. Heat-treating, with no additional activation process, PVDC can obtain a porous structure with sufficient micropores that can be used as an electric double layer capacitor with high capacitance in an aqueous sulfuric acid medium. However, when non activated PVDC-based carbon was applied for use directly in a nonaqueous EDLC, only a small value of capacitance was obtained (>5 F/g). This suggests that the accessibility of the ion in Et<sub>4</sub>NBF<sub>4</sub>/PC is hindered by relatively larger size ions than that in aqueous system. Therefore, we tried to chemically control the pore size of the PVDC-based carbon for use in a nonaqueous solvent electrolyte. As is shown, the maximum capacitance per unit volume was obtained at HTT=800 °C, which suggests that the variation of the

apparent density of the electrode should be considered as an important factor for the optimization of the electrode materials.

### **References**

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