

# STRUCTURE AND ELECTROCHEMICAL PROPERTIES OF CARBON AEROGELS WITH ACIDIC SURFACE FUNCTIONAL GROUPS

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## Introduction

Surface functional groups with oxygen on carbon electrodes in electric double-layer capacitors have been studied very often in order to understand their influences of raising capacitance values. The increase of capacitances by the oxygen-containing structure can be related to a pseudo-capacitance effect as well as an enhancement of penetration of electrolyte into electrodes, while these types of structure have been considered to hinder a stable charge-discharge performance [1]. Recently, some studies pointed out that an oxidation with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution for porous carbon materials can modify their surface properties in a different way from other types of acids [2]. It provides renewal of interest in the effect of surface functional groups on microscopic structure and electrochemical behaviors. In this study, we used carbon aerogels treated in  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution, and investigated structure of the oxidized samples with their electrochemical and electric properties.

## Experiment

All the samples were prepared from resorcinol-formaldehyde aerogel commercially available (MarkeTech International Inc.). Organic aerogels were carbonized at 1000 °C, and oxidized in 1M- or 0.1M- $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution for different periods of time. Observation with transmission electron microscope (TEM) was carried out at an accelerating voltage of 200kV.  $\text{N}_2$  adsorption isotherms of the samples were measured at 77 K to evaluate their pore structure. X-ray diffraction (XRD) patterns of the samples were obtained by  $\text{CuK}\alpha$  radiation at 40kV-80mA. Stacking structure of aromatic layers was then characterized by the Fourier transformation of carbon 002 peak. For an electrochemical characterization, cyclic voltammograms (CVs) were measured at 1.0 mV/s with a typical three-electrode test cell in 1M- $\text{H}_2\text{SO}_4$  at room temperature. Electric resistivity was estimated by a four-probe method at room temperature for the samples sliced with a thickness below 1mm.

## Results and Discussion

Amount of oxygen in the aerogel samples increased in a process of acid treatment until it reached to ca. 25wt% after 10.5 hours treatment. FT-IR spectrum of the oxidized

samples included C=O stretching vibration, indicating a presence of oxygen surface groups such as ketones or carboxyl groups. Cation-exchange capacitance estimated with  $\text{Na}^+$  was 2.5 meq/g for the samples with the maximum oxygen content.

$\text{N}_2$  surface area of the samples shown gradually decreased in the process of oxidation. Detailed analysis by the  $\alpha_S$  plot method indicated that a variation of total surface area is obviously influenced by micropore structure (Fig. 1). For a porosity of carbon aerogels, microporosity is discussed with inter-particle structure, while mesoporosity is often related to intra-particle structure. TEM observation (Fig. 2) supported the results by demonstrating very little changes in inter-particle structure among samples before and after the acid-treatment. In observations at higher magnification, we could found that primary carbon particles with less-crystalline and isotropic texture were connected each other to form network structure. Size of the particles was 5-6 nm for all the samples.

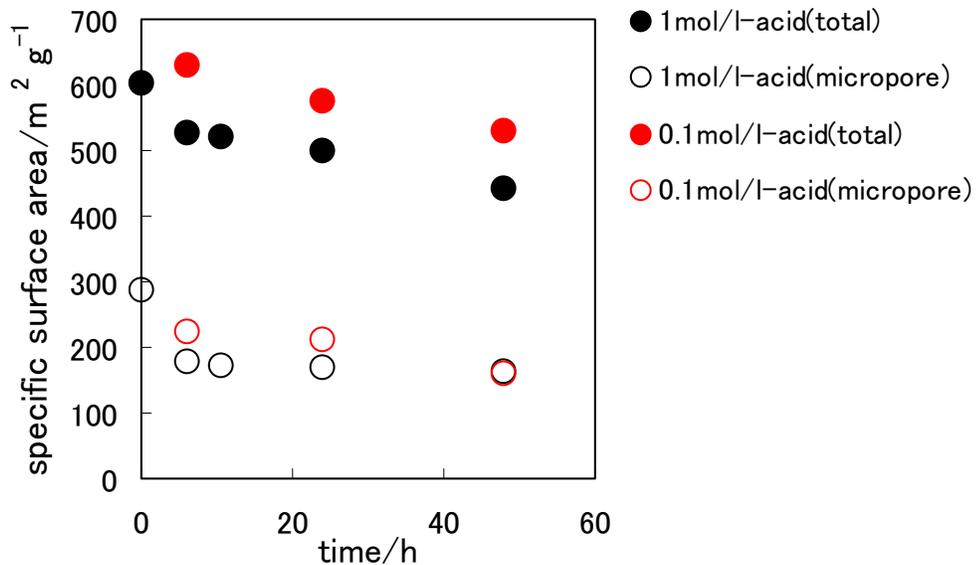


Figure 1. Specific surface area of carbon aerogels estimated by the  $\alpha_S$  plot method.

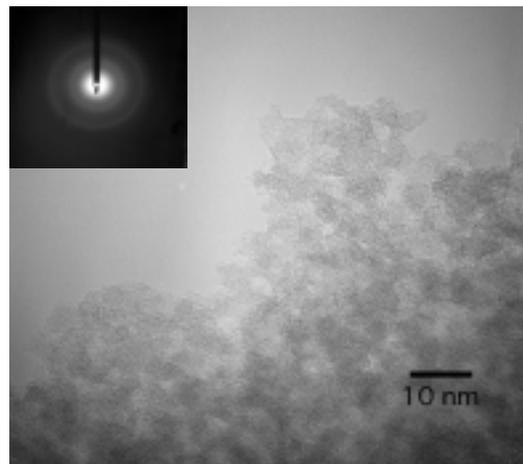


Figure 2. Typical TEM image of the acid-treated samples.

The Fourier transformation of carbon 002 reflection peaks in their XRD patterns gives structural parameters, that is, the average number of stacking layers in a stack ( $N_{ave}$ ), the average interlayer spacing ( $d_{002}$ ) and the stacking index (SI), or a parameter showing crystallinity [3]. We found that  $N_{ave}$  and SI were increased in the first 2 hours of acid-treatment, while  $d_{002}$  dropped rapidly. In the following reaction, however,  $N_{ave}$  and  $d_{002}$  were almost maintained and SI was gradually decreased. We attributed these behaviors of structure parameters to the reaction during the acid-treatment. In this process, a removal of carbons and an addition of surface functional groups can be considered as a change of structure. The former reaction would be preceded faster around disorganized carbons out of aromatic layers than around carbon atoms included in aromatic layers. This reaction can cause apparent development of stacking structure, especially at the beginning of the reaction. On the other hand, the latter would have little effect on the stacking structure itself, but can block micropores in the texture [2]. It is therefore anticipated that the former reaction is predominant early in the process of the acid-treatment, and the latter become more influential later, though both of these reactions can be preceded in the whole process.

In the CV curves in Fig. 3, the original carbon aerogel had a typical capacitive behavior in the rectangle locus. The oxidized sample showed a different shape with broad peaks. Peaks like these are often related to the electrochemical reaction of quinone groups, which seems agree with the result of FT-IR measurement showing the presence of CO bonding. Capacitances estimated from these CVs jumped up largely by oxidation to 180 F/g.

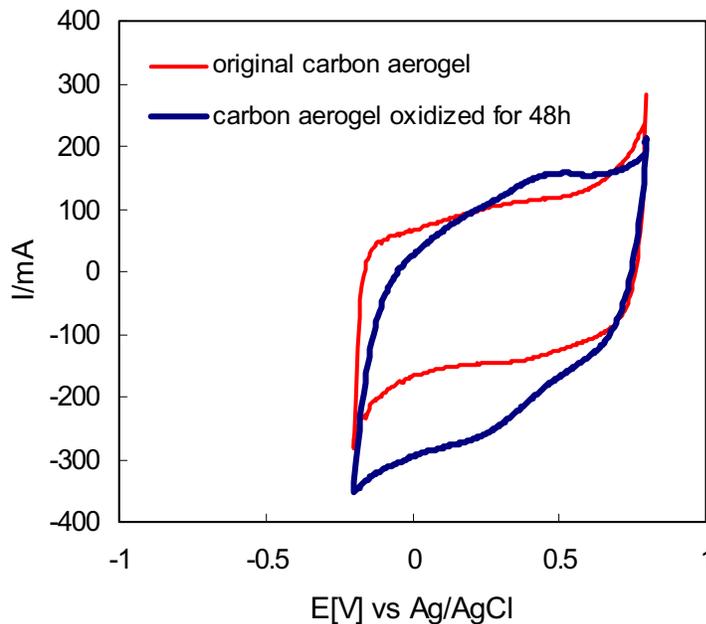


Figure 3. Cyclic voltammogram curves for the carbon aerogels.

Electric resistivity  $\rho$  of the oxidized samples was estimated by the equation:

$$\rho = 4.5324w V/I, \quad (1)$$

in which  $V$  is a voltage at a current  $I$ , and  $w$  is a thickness of a sample plate. Resistivity  $\rho$  of the carbonized samples before the oxidation was  $0.07 \Omega \text{ cm}$ , which agreed well with the result in the earlier study for carbon aerogel samples with the similar density. For the acid-treated samples,  $\rho$  was obviously proportional to the amount of oxygen. Surface functional groups such as  $\text{C}=\text{O}$  could work as acceptor creating holes [4], and therefore the result is reasonable. In relation to the network structure of carbon aerogels, transport properties has been related to the charge transfer processes, or carrier hopping, between the primary particles, and defects internal to the particles were not considered to play as significant a role as the particles themselves [4]. But in this study,  $\rho$  values were significantly increased due to the modification of intra-particle structure. It implies the strong influence of oxygen-containing functional groups on the behavior of electrons in the carbon aerogels.

### Conclusions

Carbon aerogels oxidized in  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution indicated structural changes based on a removal of disorganized carbons and an addition of surface functional groups. These changes were more obvious in intra-particle structure of primary particles in the carbon aerogels, while inter-particle network structure typically observed for carbon aerogels were maintained. Electric capacitance behaviors and electric resistances of the samples could be related to the degree of oxidation for the samples.

### References

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