

PORE STRUCTURE AND CAPACITOR PERFORMANCE OF N-ENRICHED CARBON FOAM

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Introduction

Nitrogen-enriched carbons are now regarded as a noteworthy candidate for supercapacitor electrode. Substitutionally placed nitrogen atom in carbon framework can display notable additional capacitance (~200F/g) based on the faradaic mechanisms especially in acid medium. Moreover, an exceptionally high cyclic durability can be realized despite the pseudo capacitive regime. The origin of such a high capacitance of N-enriched carbon seems to be due to the interaction between proton and nitrogen atom. However, this explanation is not wholly convincing. Actually, this sort of carbon also develops rather high capacitance in alkaline electrolytes. The capacitance is not so high as in acids, but beyond expectation.

Another remarkable feature of N-enriched carbon electrode is less indispensability for pore structure. The capacitance obtained using N-enriched carbons is often very far from the value expected by its BET specific surface area estimated by nitrogen adsorption at 77K (BET-SSA-N₂) which is practically standardized method for evaluation of porous electrode materials. Even if taking into account the electrochemical interactions, the obtained capacitance per unit surface area is abnormally enormous. This fact compels us to find persuasive argument. Accordingly, in the present system, we should notice that BET-SSA-N₂ is not always comparable for the effective surface area of porous electrodes.

For several years, we have been interested in electrochemical performance of a series of nitrogen-enriched carbons prepared from nitrogen containing organic precursors by carbonization [1-4]. Recently, we have reported N-enriched carbon foams can be realized by the carbonization of melamine foams, which are mass-produced as washing sponge [5]. The obtained carbon foams appeared representative electrochemical properties of this sort, for instance, almost rectangular shape of cyclic voltammograms and high capacitance going up to over 250F/g. In this way, the carbon foam can be considered as a suitable electrode material for discussing the electrochemistry of N-enriched carbon into details; besides good productivity and convenient handling are advantageous factor from an experimental aspect. The present study describes electrochemical properties of N-enriched carbon foam mainly from the viewpoint of the surface characteristics of electrode.

Experimental

Commercially available melamine foam (which are mass-produced under the patent claimed by BASF GmbH) was cut from a cuboidal block to an adequate size and subjected to carbonization at 600-1200°C for 60min in an inert atmosphere. The microstructure of the obtained samples was observed by FESEM and TEM under operating at 1kV (for SEM) and 120kV (for TEM) acceleration voltages. Elemental analysis was conducted using CHN coder (combustion method). And adsorption isotherms were recorded using an automatic adsorption apparatus.

For the electrochemical measurements, the obtained samples need not to be molded to the conventional pellet electrode, because of its elasticity. Consequently, we can apply the samples for the capacitor electrode without any additives such as carbon black for a conductive agent and fluorocarbon polymers for a binder. Precisely weighed piece of the carbon foam was assembled into the working electrode for three or two electrode cell equipment by insertion between Pt-mesh and glass fiber paper and then by fastening with two Teflon plates. The electrochemical performance of each sample was evaluated in 1M H₂SO₄ aqueous solution and other electrolytes solutions by cyclic voltammetry (CV) and galvanostatic charge/discharge cycling (GC). For CV, the potential range was -100~900mV (vs. Ag/AgCl) and scan rate was mainly 1mV/s. The GC was cycled between -100 and 900mV (vs. Ag/AgCl) at a constant current of 20-1000mA/g.

Results and discussion

Figure 1 shows a scanning electron micrograph of carbonized melamine foam at 800°C. The branched fibers with a diameter of several micrometers are entwining each other. The cross section of each fiber shows a triangular shape. This basic structure certainly originated in that of pristine melamine foam. This is because the carbonized melamine foam could keep its resilience even after the heat treatment with a large amount of weight loss and shrinkage. The carbonization yields of melamine foam were ca. 15wt% (800°C) and ca. 7wt%(1200°C). Almost 20wt% of nitrogen remained in the foam after heat

treatment at 800°C, then decreased with HTT. Approximately 7wt% of nitrogen still remained at 1000°C. The residual nitrogen content was sensitive to not only HTT but also residence time.

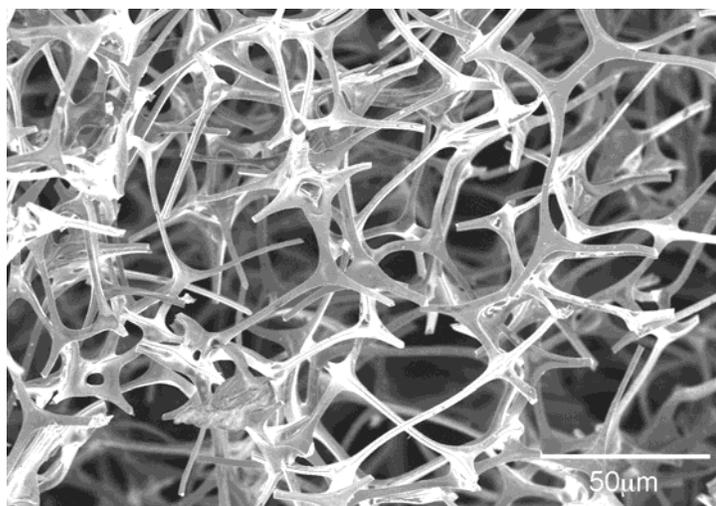


Figure 1. Scanning electron micrograph of carbonized melamine foam (800°C, 60min).

Cyclic voltammogram measured in 1M H₂SO₄ using N-enriched carbon foam prepared at 800°C is displayed in Fig.2. The voltammogram shows almost rectangular curve with no distinct peaks. The gravimetric capacitance was found from calculation to be 245F/g at 0.4V. The result on galvanostatic charge/discharge cycles demonstrates correct and reproducible curve, and gave 200-300F/g of high capacitance. Meanwhile, nitrogen adsorption onto the carbon foam was not measurable owing to its nonporous characteristics for nitrogen molecules (0.364 nm in diameter) at the liquid nitrogen temperature. Hence, we can regard the BET surface area of carbon foam as a negligible value. It may be equal to geometrically estimated surface area (<1m²/g). Such an enhanced capacitance is certainly attributed to the functionality of residual nitrogen in analogy with other N-enriched carbons. One of the conceivable mechanisms for this pseudo capacitance is proton involvement in the charge-discharge process as described in Fig.3. This kind of redox interaction by proton is known as a reaction having excellent reversibility and cyclic durability. And, high power density can be realized owing to rapid migration of proton in aqueous solutions. In this way, the protonic interactions with N-enriched carbons can be regarded as one of promising way to give pseudo capacitance to the supercapacitors.

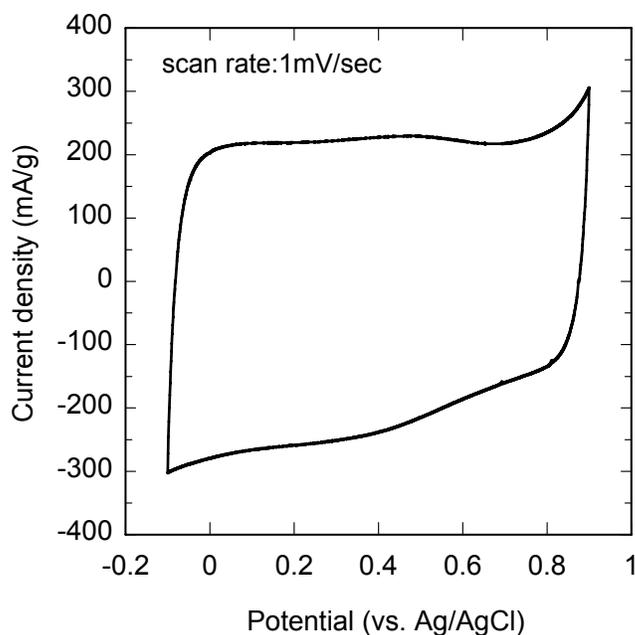


Figure 2. Cyclic voltammogram of N-enriched carbon foam prepared at 800°C in 1M H₂SO₄.

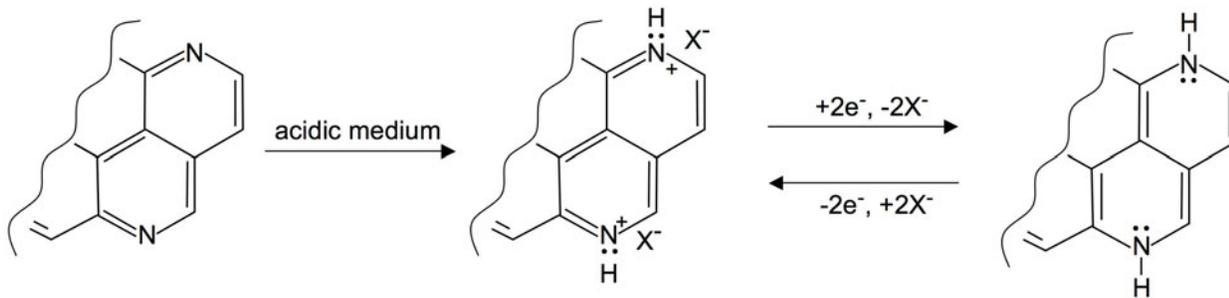


Figure 3. Possible example of the reaction between proton and nitrogen atom in carbon.

As for a proton, smallest chemical species, we can understand that it can penetrate into the apparently nonporous carbon judged by nitrogen molecules at low temperature. Even so, there is a doubt that overall electrochemistry of this material can be accounted by the protonic interactions. The high capacitance in alkaline electrolytes cannot be expressed certainly. On the other hand, in neutral solutions such as Na_2SO_4 and NaCl , though much lower than in acids, almost 100F/g of capacitance with rectangular shape of CV still remains. This capacitance may be due to genuine electric double layer adsorption, indicating N-enriched carbon foam is not nonporous against not only protons but also other aqueous ions including cations and anions. In other word, aqueous ions, whether cation or anion and whether hydrated or not, can get into the pores having less than 0.364nm in diameter located on the surface of N-enriched carbon foam. Of course, it should be noticed that this rough argument lacks effect of diffusion, etc. Consequently, the validity of BET-SSA- N_2 is extremely limited for the N-enriched carbon foams.

To estimate the proportionate surface area to the capacitive performance of the carbon foam, adsorption measurements of water at 298K and carbon dioxide at 298K and 195K have been carried out. Contrary to the nitrogen adsorption, in all cases, certain amount of molecules could adsorb into the pore of the carbon foam. Especially, adsorption of carbon dioxide at 195K, enabled us to calculate BET surface area (BET-SSA- CO_2 -195K), revealed probable effective surface area for aqueous electrolytes. It gave reasonable value of capacitance per unit surface area for neutral salts, viz. 0.2~0.3F/m². In such a way, a survey of electrochemistry of N-enriched carbon foams through the gas adsorption measurements will be presented in detail at the conference.

References

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