

Electrochemical properties of Nitrogen-enriched Carbon Aerogels

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INTRODUCTION

We have reported that nitrogen-enriched carbons have a high capacitance per unit surface area, though the mechanism is still unclear [1]. Carbon aerogels have been extensively studied due to its distinguished characteristics which are attributed to the large mesoporosity. The mesoporous structure and the specific surface area more than 300 m²/g are maintained up to 3000 K [2]. The mesoporous structure with less microporosity is preferable to know the effect of hetero atoms substituted into graphene layers because the double layer capacitance is changed by the size correlation between micropores and ions [3]. In the present study, nitrogen-enriched carbon aerogels were prepared and the properties were evaluated as an electrode for electric double layer capacitors.

EXPERIMENTAL

Melamine-formaldehyde aerogels prepared by sol-gel polymerization were used as the precursor of nitrogen-enriched carbon aerogels [4]. The organic aerogels were carbonized at 1173, 1273 and 1473 K for 1 h under an inert atmosphere. The samples were represented as MFCAG-1173, 1273 and 1473, respectively. Carbon aerogels derived from resorcinol-formaldehyde resins (RFCAG) without nitrogen atoms in the precursors were used for comparison.

RESULTS AND DISCUSSION

The nitrogen adsorption isotherms of MFCAGs were of Type IV according to the IUPAC classification, which has a hysteresis loop in adsorption/desorption branch indicating the development of mesoporous structure. The analysis by means of α_s -plot revealed that mesopores offer the majority of surface area in MFCAGs; the mesopore surface area occupies 76 and 86% of the specific surface area in MFCAG-1273 and 1473, respectively. A considerable amount of nitrogen atoms are remained in MFCAGs (Table 1). The N 1s X-ray photoelectron spectroscopy (XPS) spectra (Fig. 1) indicate that the nitrogen atoms are substituted in MFCAGs as forms of pyridinic nitrogen (nitrogen bonded to two sp² carbon atoms in a graphene layer) at the binding energy of 398 eV and quaternary nitrogen (nitrogen bonded to three sp² carbon atoms) at 401 eV. The MFCAG-1173 has higher peak intensity of nitrogen than quaternary nitrogen, while the latter becomes higher at higher heat-treatment temperatures.

The cyclic voltammograms measured in 1M H₂SO₄ are shown in Fig. 2. The specific capacitance, SC, of MFCAG-1273 is about twice that of MFCAG-1473, in spite of few changes in the porosity parameters. The relation between nitrogen content and the capacitance per unit surface area, SC/S_A_{BET}, shows that the nitrogen substituted into graphene layers causes an increase of SC/S_A_{BET} (see Table 1). The results suggest some pseudocapacitance by the existence of pyridinic nitrogen which has a lone pair, being on the edge of a graphene layer.

REFERENCES

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Table 1. Nitrogen content, BET surface area, specific capacitance and capacitance per unit surface area.

Sample	N (wt%)	S _A _{BET} (m ² /g)	SC (F/g)	SC/ S _A _{BET} (F/cm ²)
MFCAG-1173	24.86	810	235	0.32
MFCAG-1273	14.66	800	205	0.27
MFCAG-1473	2.40	818	107	0.14
RFCAG-1273	0	1036	148	0.14

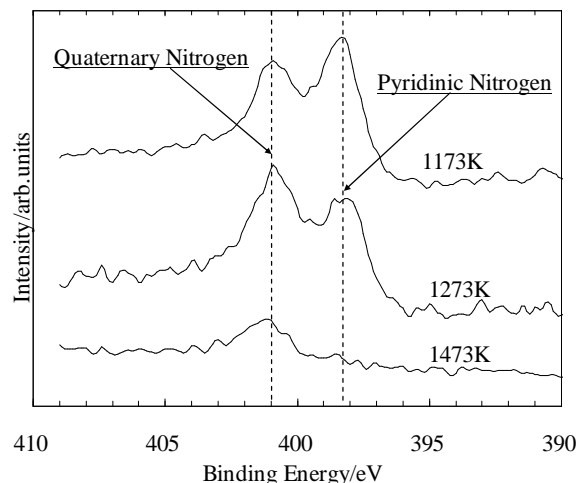


Fig. 1. N 1s XPS spectra of MFCAGs.

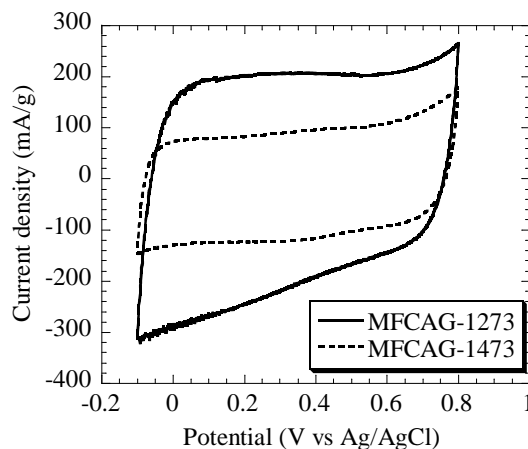


Fig. 2. Cyclic voltammograms in 1M H₂SO₄.