

Nanocarbons as electrode materials for electrochemical capacitor

Yasushi Soneda

National Institute of Advanced Industrial Science and Technology (AIST),
Energy Technology Research Institute
16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
y.soneda@aist.go.jp

Electric double layer capacitor (EDLC) using carbon electrodes have been anticipated as an energy storage device for electric vehicle, distributed energy system applications and so on. High surface area carbons were employed for the electrode materials of EDLC to store energy in the electric double layer, and the control of pore size distribution of its carbons was recognized to be very important [1-3]. On the other hand, when the electrode material shows Faradic reactions at the electrode surface in wide range of potential window, the energy stored by the charge transfer can be accounted as pseudo-capacitance. This type of energy storage is found in transition metal oxides, conducting polymers and intercalation reaction with carbons, and called as the electrochemical capacitor [4].

Although the high energy density type capacitor using organic electrolyte has been mainly targeted in recent years, the aqueous electrolyte capacitor has several advantages such as wider working temperature, high power density due to the higher electrical conductivity and definitively easier fabrication in the industrial factory. However, the energy density of capacitor with aqueous electrolyte is restricted by its smaller working voltage window (decomposition limits of water). Therefore, the investigation of novel carbon materials with high energy density is strongly demanded for the electrochemical capacitor with aqueous medium.

We have been synthesized various kinds of novel nanocarbons and found that nitrogen-enriched carbon derived from melamine possesses high capacitive values in spite of lower surface area [5, 6]. Recently, MgO template method has been developed to prepare mesoporous carbon with high specific surface area (ca. $1500\text{m}^2/\text{g}$) by simple carbonization of mixture of carbon precursor compounds and Mg containing organic salt, such as Mg acetate [7]. In this study, we have tried the synthesis of nitrogen enriched porous carbon by using melamine and magnesium citrate as precursors for N-enriched carbon and MgO template, respectively. The resultant N-enriched porous carbons were characterized by gas adsorption, elemental analysis and electrochemical tests.

The samples were prepared following procedure. Prescribed amount of melamine ($\text{C}_3\text{H}_6\text{N}_6$) and magnesium citrate ($\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 9\text{H}_2\text{O}$) were mixed well using mixing rotator for 3hrs and then heat treated in nitrogen flow at $800\text{ }^\circ\text{C}$ for 1hr (heating rate of $5^\circ\text{C}/\text{min}$). Carbonized solid was immersed in 6M HCl for overnight to dissolve MgO particles in products and washed with distilled water. For the electrochemical measurements, the sample carbons (ca. 10mg), binder PTFE and carbon black were mixed with the weight ratio of 8:1:1 and pressed into a disk (1cm diameter). A disk specimen was placed in home-made holder (PTFE plate) and used as working electrode. Counter and reference electrode were platinum mesh and Ag/AgCl, respectively. 40% H_2SO_4 was used as electrolyte.

Figure 1 shows the relation between carbon yield and precursor mixing ratio. Carbon yield at the melamine/MgO ratio of 0 and 10 imply the residue from Mg citrate and melamine, respectively. Pure melamine monomer vaporizes around $300\text{ }^\circ\text{C}$ and never produce solid product (melamine/MgO=10). Mg citrate gave 33 % of carbon after carbonization and acid treatment.

From Figure 1, it is clearly shown that all the mixture gave higher carbon yield by co-pyrolysis than expected one from mixing ratio.

Specific surface area and elemental analysis of some samples are listed in Table 1. In the case of sample 2 (melamine/MgO ratio = 7/3), the carbon yield of 42.4% was obtained which was higher than the one of Mg citrate (32.6%), and the specific surface area (1015 m²/g) was closed to only half of one from Mg citrate (2182 m²/g). Elemental analysis showed quite high value of nitrogen (13.4 wt%) in sample 2. Though the values of carbon yield and specific surface area for sample 3 were almost similar with sample 4 (Mg citrate), 1.2 wt% of nitrogen was incorporated.

Electrochemical capacitor results using these samples will be shown at symposium.

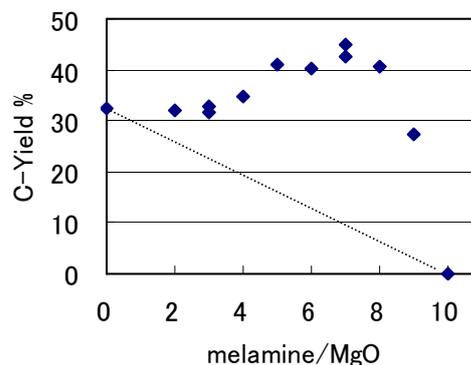


Fig.1 Dependence of carbon yield on mixing ratio of melamine/MgO.

Table 1 Characteristics of carbonized sample with different precursor ratio.

	precursor ratio		carbon yield %	SA(BET) m ² /g	elemental analysis (wt%, daf)			
	melamine	Mg citrate			C	H	N	O (diff)
sample 1	10	0	0.0	-	-	-	-	-
sample 2	7	3	42.4	1015	73.7	1.5	13.4	11.4
sample 3	3	7	32.7	2014	89.2	0.9	1.2	8.7
sample 4	0	10	32.6	2182	93.1	0.9	0.0	6.0

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