Electric Double Layer Capacitance Properties of Porous Carbon Nanofibers Prepared by Polymer Blending Technique

Soshi Shiraishi and Asao Oya Department of Nano-Materials Systems, Graduate School of Engineering, Gunma University Kiryu, Gunma 376-8515, Japan E-mail: ssiraisi@chem.gunma-u.ac.jp

Porous nano-size carbons with high specific surface area are very attractive as electrode of electric double layer capacitor (EDLC). We prepared porous carbon nanofibers with high specific surface area by the polymer blending technique. Novolac-type phenolic resin (PF) as carbon precursor polymer and polyethylene (PE) as pyrolyzing polymer without carbon residue were blended to obtain the polymer blend with the mixing ratio of 3:7 by weight. The PS/PE blend polymer was spun, carbonized, and steamactivated at 800°C as illustrated in **Fig.1**. The resulting carbon fibers were the microporous carbon nanofibers with around 100 nm diameter (**Fig.2**) and 1000 ~ 2000 m²g⁻¹ in BET specific surface area.

The capacitance advantage of the highly porous carbon nanofibers (HP-CNFs) compared with conventional activated carbon fibers (ACFs) were observed when using organic electrolyte such as propylene carbonate solution, but it is not so remarkable [1]. However, HP-CNFs showed prominent effect on the capacitance in gel electrolyte. HP-CNFs indicated higher capacitances in the methacrylatebased gel electrolyte (plasticizer; propylene carbonate) than ACFs at comparable specific surface area (Fig.3). The capacitance advantage of HP-CNFs was more prominent in the Li⁺ cation adsorption than BF_4 anion. The results of N₂ adsorption measurement showed that the pore structure of HP-CNFs was similar to that of ACFs. It means that the nano-size of HP-CNF produces the enhancement of the capacitance. Our previous results revealed that the ion adsorption in the double layer is strongly suppressed by the ion sieving effect of micropores with narrow micropores [2]. That effect can be easily expected more serious in the case of gel electrolyte due to its high viscosity and low liquidity. Therefore, it can be said that the higher capacitance for HP-CNF in the gel electrolyte is derived from the shorter path of micropores, in which the ion sieving effect was effectively relaxed. The nano-sizing of porous carbon materials is effective in enhancement of the double layer property, especially, in gel electrolyte.

References

1) S. Shiraishi, H. Kurihara, and A. Oya, Carbon'03, An International Conference on Carbon, extended abstract, Poster, Thursday, 2.23.

2) S. Shiraishi, H. Kurihara, L. Shi, T. Nakayama, and A. Oya, *J. Electrochem. Soc.*, **149**, A855-861 (2002).



Figure 1 Schematic illustration for the preparation method of highly porous carbon nanofiber (HP-CNF) by polymer blend technique.



Figure 2 Transmission electron micrograph (TEM) of HP-CNF .



Figure 3 Correlation between BET specific surface area (BET-SSA) and double layer capacitance (galvanostatic : 40 mAg⁻¹) for HP-CNFs and ACFs in 0.5M LiBF₄/ methacrylate-based gel electrolyte. (a) cation adsorption capacitance ($3 \rightarrow 2$ Vvs.Li/Li⁺), (b) anion adsorption capacitance ($3 \rightarrow 4$ Vvs.Li/Li⁺).