

Synthesis of Three-Dimensionally Macroporous Hard Carbon Materials as Electrode and Characterization of Their Electrochemical Properties

Sei-ichiro Tabata, Masayoshi Watanabe

Department of Chemistry & Biotechnology, Yokohama National University and CREST-JST
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

The control of electron transfer at the electrode/electrolyte surfaces as well as the ionic conduction in the electrolyte is a fascinating domain of current research for their significant importance in electrochemical systems. In order to raise the efficiency of electrochemical devices, the electrode/electrolyte interfacial resistance should be reduced. Nano-fabrication of electrode materials, which can realize fast charge transfer at the electrode/electrolyte interfaces, is therefore, considered to be useful means for the realization high performance electrochemical devices.

Macroporous materials, fabricated by using colloidal crystals consisting of mono-dispersed particles as templates, are the subject of intense study in the past few years, for their photonic bandgap structures. It is also possible to have the macroporous electrode materials composed of inorganic metal, polymer and carbon¹⁾⁻³⁾. The nano-ordered three-dimensionally periodic pore structure contributes not only to enlarging surface area per unit volume but also to the formation of electron and ion conductive paths. In this work, we aimed at synthesizing novel carbon material, which can be potentially used as electrodes in electrochemical systems, since the control of the electron-transfer at the electrode/electrolyte surfaces seems to be possible by using such macroporous electrodes.

Aqueous solutions containing mono-dispersed silica spheres in the range of 100 nm - 1 μm were slowly filtrated through nitrocellulose filtration membrane under a reduced pressure. The colloidal crystal was heated at 1000 °C to sinter the silica. A mixture of furfuryl alcohol and oxalic acid (= 1:0.005 by weight) was added into the void space of the colloidal silica templates and then heated at 80 °C for 3 days to obtain polyfurfuryl alcohol resin-silica composites. The composites were then heat-treated at 900-1100 °C for 1h to carbonize the resin in the void space of silica (heating rate at 5°C/min). Successively, the silica particles in the carbon-silica composites were etched off with aqueous HF to dissolve the silica. After washing, the surface of the carbon was observed by SEM. The image of the carbon (Fig. 1) indicates the periodic structure that reflects the structure of the template silica crystal. X-ray diffraction data indicates that the amorphous structure is consistent with glassy carbon.

The three-dimensionally macroporous electrodes were used in electrochemical measurements. Fig. 2 shows a typical cyclic voltammogram using a macroporous carbon electrode in an acetonitrile solution containing 0.1 M LiClO₄ and 5mM ferrocene. The cyclic voltammogram indicates large background current due to the double-layer capacitance. Furthermore, the capacitive background current increases much larger than the faradaic current as the scan rate is increased. The peak separation is about 59 mV at a scan rate of 20 mV/s. We will discuss detailed electrochemical properties of the porous carbon electrodes in this presentation.

Acknowledgment

This work was supported by CREST of Japan Science and Technology (JST).

References

- [1] B. T. Holland, C. F. Blanford, A. Stein, *Science*, **281**, 538 (1998)
- [2] Y. Takeoka, M. Watanabe, *Adv. Mater.* **15**, 199 (2003)
- [3] A. A. Zakhidov, R. H. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S. O. Dantas, J. Marti, V. G. Ralchenko, *Science* **282**, 897 (1998)

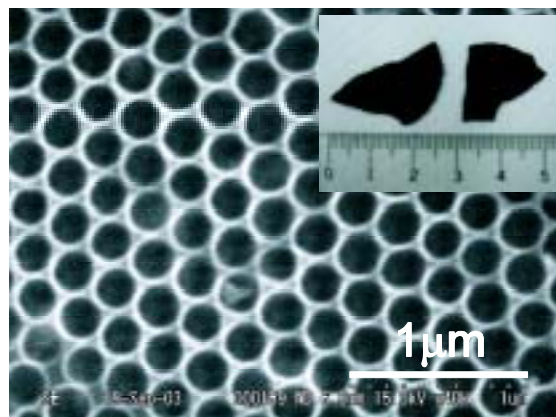


Fig. 1 SEM image of three-dimensionally porous carbon derived from polyfurfuryl alcohol resin.

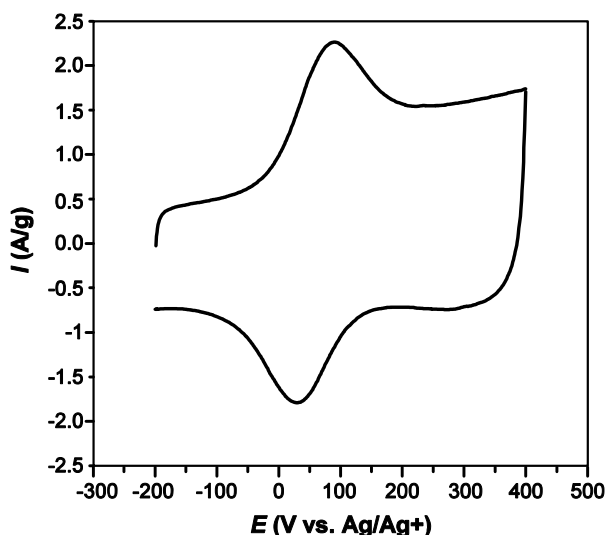


Fig. 2 Cyclic voltammetry obtained with 500 nm silica colloidal crystal templated macroporous electrode in 0.1 M LiClO₄ acetonitrile solution containing 5 mM ferrocene at scan rate of 20 mV/s.