Designing of super carbon materials for ionic liquid-based supercapacitors by template carbon method

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The sustainability of modern society calls for a mart utilization of electric power, and therefore energy storage devices including batteries and supercapacitors are intensively investigated to support it. In this research, we developed a new understanding and new materials for supercapacitors.

1. The electrochemical degradation of an ionic liquid was investigated using a variety of carbon materials including carbon blacks, activated carbons, zeolite templated carbon, and mesoporous templated carbon. The carbon basal plane was found to be involved in the degradation reactions.

2. The structure of a mesoporous templated carbon was controlled to have different graphene stacking numbers and various amounts of nitrogen doping. It is found that the capacitance has a quantum origin and we successfully quantified the quantum capacitance for a full understanding of the origin of capacitance. Furthermore, the nitrogen-doped mesoporous templated carbon shows enhanced quantum capacitance and a good overall performance in ionic liquid-based supercapacitors.

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ionic liquid templated carbon supercapacitors

(1) The applications of supercapacitors are presently restricted in limited fields because of the low energy density (E). Enhancing the stability of supercapacitors is effective to increase E by having the system work with a wider operation voltage (U) according to the formula, $E = CU^2/2$. Ionic liquids draw a lot of attention for fabricating high-voltage supercapacitors due to their intrinsically better stability than conventional organic electrolytes. However, so far it is still unclear how degradation happens in the case of ionic liquids and what is the role of carbon during this process.

(2) Our group previously reported a highly stable mesoporous templated carbon which is promising as an electrode material for ionic liquid-based supercapacitors. However, the capacitance of this carbon material is limited. Moreover, the value of capacitance is variable depending on the applied potential. Such a capacitance behavior worth to be investigating and modification of the carbon structure is necessary to further enhance the capacitance.

(1) The first purpose of this research is to interpret the degradation mechanism of ionic liquid.

(2) The second purpose is to understand the limiting factor of the capacitance of a mesoporous templated carbon.

(3) The third purpose is to synthesize a carbon material for ionic electrolyte-based supercapacitors to achieve both high values of operation voltage and capacitance.

(1) To understand the effect of the carbon surfaces on the degradation of ionic liquids used in supercapacitors, a correlation study was done to relate the quantified carbon basal plane/carbon edges with electrochemical degradations.

(2) The structure of a mesoporous templated carbon was controlled to have different graphene stacking numbers and various amounts of nitrogen doping by changing the chemical vapor deposition and post-annealing conditions.

(3) The carbon structures and electrochemical performance were investigated by various techniques including cyclic voltammetry, nitrogen physisorption, X-ray diffraction, Raman spectroscopy, and a high-temperature-programmed desorption method up to 1800 °C. Various electrolytes were used in this study: an organic electrolyte of 1 M tetraethylammonium tetrafluoroborate (Et_4NBF_4) dissolved in propylene carbonate and four ionic liquids including 1-Butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$), 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI), 1-Ethyl-2,3-dimethylimidazolium Bis(trifluoromethanesulfonyl)imide (EDMIMTFSI), and 1-Ethyl-3-methylimidazolium Tetrafluoroborate ($EMIMBF_4$).

(1) We measured the cyclic voltammetry curves of various carbon materials including two carbon blacks (XC72 and KB), four activated carbons (YP50F, AACH2, AAC, and MSC30), zeolite templated carbon (ZTC), and a mesoporous templated carbon (GMS) in an ionic electrolyte of $BMIMBF_4$. The results (Figure 1) suggest the carbon basal plane was involved in the electrochemical degradation.

(2) We modified the graphene stacking numbers of GMS by changing the time period of chemical vapor deposition from 2 to 4 and 6 h. The average graphene stacking was controlled from 1.5 to 1.9 and 2.9. Figure 2a shows the structure model of GMS with near-single layer graphene. The corresponding BET surface area values were determined to be 1770, 1390, and 898 m^2 g^{-1}, respectively. The electrochemical results suggest increasing graphene stacking indeed slightly enhances
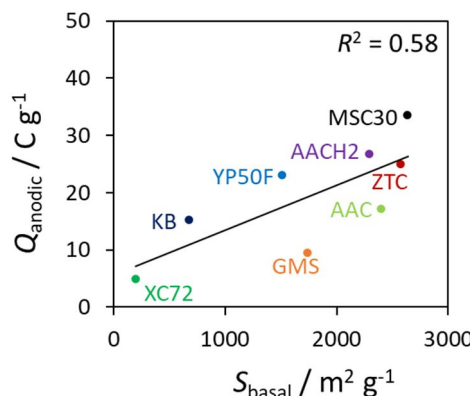

Figure 1. The plot of anodic charge versus carbon basal plane surface area.

the areal capacitance, however, such an increase cannot compensate for the decrease of specific surface area.

(3) We confirmed the capacitance of GMS has a quantum origin that results in a "butterfly-shaped" cyclic voltammetry curve and we successfully quantified the quantum capacitance (Figure 2b) for a full understanding of the origin of the cap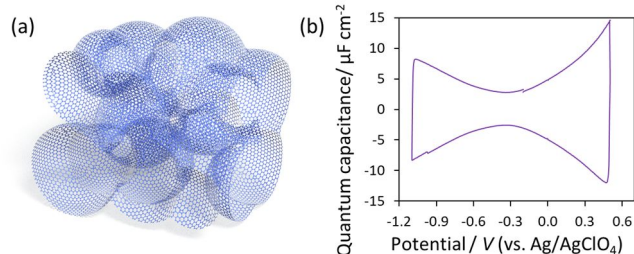acitance of this material. Indeed, to the best of our knowledge, this is the first study to experimentally demonstrate that quantum capacitance is a limiting factor for the overall capacitance of 3D graphene-based carbon materials.

Figure 2. (a) The structure model and (b) The calculated quantum capacitance of GMS.

(4) We successfully synthesized nitrogen-doped mesoporous 3D graphene materials (named N-CMS) by chemical vapor deposition of acetonitrile on a template of Al_2O_3 nanoparticles. The nitrogen content can be controlled by
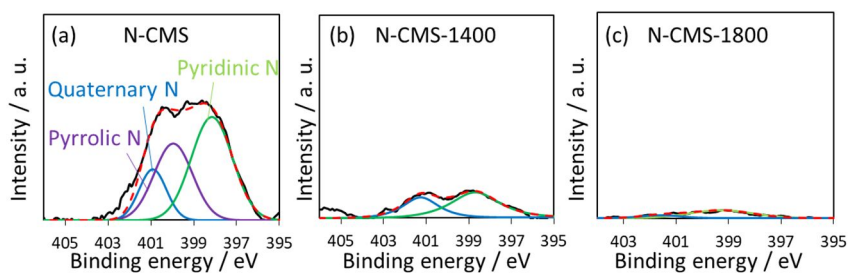

Figure 3. X-ray photoelectron spectroscopy results of (a) N-CMS and the samples heat treated at (b) 1400 and (c) 1800 °C.

further heat-treatment at various temperatures from 1000 to 1800 °C. The elemental analysis results suggest the material synthesized through chemical vapor deposition has a high nitrogen content of 9.3 wt%, while further heat-treatment can decrease the value to only 0.2 wt% (1800 °C). X-ray photoelectron spectroscopy suggests quaternary N, pyrrolic N, and pyridine N were doped (Figure 3a). Additionally, pyrrolic N was thermally decomposed at a lower temperature during the heat treatment (Figures 3b and 3c). These nitrogen-doped mesoporous 3D graphene materials have high specific surface areas of over 2000 m^2 g^{-1}. This highly developed porosity was kept even after heat-treatment at a high temperature of 1800 °C.

(5) It is found that nitrogen doping can enhance the capacitance of 3D graphene. Moreover, a transformation of the shape of cyclic voltammetry curves from "butterfly-shaped" to "rectangular-shaped" was observed with an increase in the nitrogen content. Such a transformation is ascribed to the enhancement of quantum capacitance.

(6) We used nitrogen–doped mesoporous 3D graphene materials in four different types of ionic electrolytes. The shape of cyclic voltammetry curves is "rectangular-shaped" (Figure 4) due to the nitrogen-doped structure. The highest working voltage can be 4.0 or 4.3 V, depending on the electrolyte. By electrochemical impedance measurement, it is found that EMIMTFSI and EDMIMTFSI show smaller impedance compared with BMIMBF$_4$ and EMIMBF$_4$.
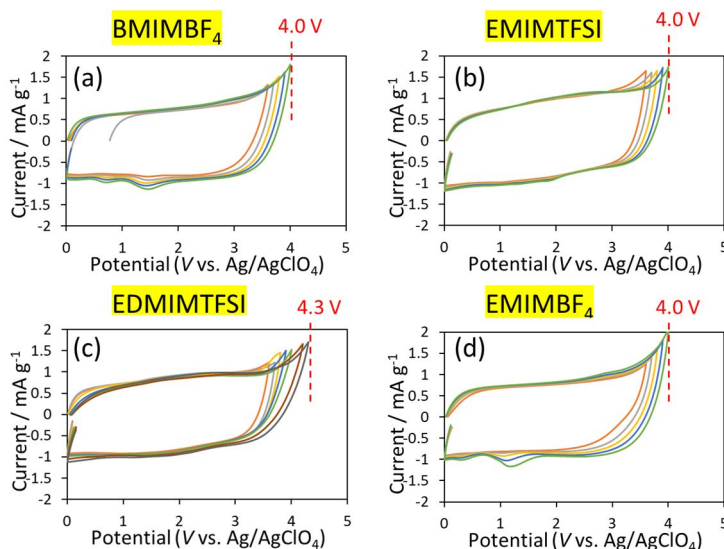

Figure 4. Cyclic voltammetry curves of N-CMS in ionic electrolytes of (a) BMIMBF$_4$, (b) EMIMTFSI, (c) EDMIMTFSI, and (d) EMIMBF$_4$.

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