PREPARATION AND EVALUATION OF POLYAMINE-DERIVED NITROGEN-DOPED POROUS CARBON

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Introduction

The nitrogen doping of carbon can improve conductivity and lead to a reversible pseudocapacitive reaction of an electrolyte that enhances the specific capacitance of the carbon. Thus, many reports on capacitance improvement via nitrogen doping have been published. This nitrogen-doped carbon is prepared via carbonization of a polymer compound containing nitrogen. In this study, nitrogen-doped porous carbon was produced using penta-ethylenehexamine (PEHA) as a carbon and nitrogen source and $FeCl_3$ as a catalyst. $FeCl_3$ was used to promote graphitization and enable carbonization at low temperature and in a short duration. The obtained carbon material, which is a porous carbon with relatively high crystallinity, exhibits high nitrogen content. Using this obtained carbon, when the electrostatic double-layer capacitance (EDLC) performance was evaluated, the capacitance per unit mass in the sulfuric acid electrolyte solution was 190 F/g (current density at 50 mA/g), and its electrode exhibited a high specific capacitance of 0.66 F/ cm^2 per unit area, indicating the effects of nitrogen doping. Then, using poly-vinyl-alcohol (PVA) as a comparative material, the influence of the carbon source on the crystallinity and surface properties was assessed to investigate the effect of iron catalyst and nitrogen.

Materials and Methods

PEHA and PVA (n ≒ 2000) were used as a carbon sources and ferric chloride (Ⅲ) was used as a catalyst. The carbon source and the catalyst were mixed with a mass ratio of 3:2, and three type of carbon precursor (i.e. only PEHA, PVA and PEHA/PVA) were prepared as carbon sources. These carbon precursors were carbonized under N_2 atmosphere at 900 ^{o}C for 3 min. The obtained carbon materials were treated in 10 % H_2SO_4 at 60 ^{o}C for 2 h, then vacuum dried at 110 ^{o}C for 24 h. Crystallinity identification and evaluation were performed by using X-ray powder diffraction [XRD, Rigaku Ltd.]. Further, the surface properties were evaluated at 77 K using nitrogen gas adsorption and desorption measurement [Autosorb-3B, Quantachrome instrument Japan]. Elemental analysis was performed via X-ray photoelectron spectroscopy [XPS, Quantum-2000, Ulvac-Phi Co., Ltd.]. The EDLC electrode was prepared by mixing carbon material, acetylene black and PTFE at a weight ratio of 8:1:1, respectively. EDLC characteristic were evaluated on a tripolar-type cell with H_2SO_4 aqueous as electrolyte. The galvanostatic constant-current charge-discharge measurements were performed within the range of 50 – 1000 mA/g. In addition, the electrostatics capacitance was calculated within the range of 0.2 – 0.8 V.

Results and Discussion

Fig. 1 shows the XRD patterns of the acid treated carbon materials post heat treatment carbonization. All the samples display the diffraction patterns at 2 θ = 26 ^{o}, corresponding to the *002* diffraction of the graphite. Furthermore, a partially laminated carbon hexagonal network surface is also presented herein. Owing to the catalytic effect of iron chloride, thermal

decomposition occurs at a low temperature through the dehydrogenation reaction to form an aromatic ring, following which the amorphous carbon forms. Therefore iron particles derived from iron oxide dissolve the amorphous carbon, followed by the moving of the iron particles while the graphitic carbon precipitates. Presumably, the partially crystallized samples were obtained in this manner. Furthermore, iron chloride, which was added as a catalyst to promote carbonization, influenced PVA and PEHA. Fig. 2 shows the N_2 adsorption and desorption isotherms of the carbon materials obtained from PVA/PEHA mixed sample and the sample in which PEHA was used as a carbon source. The PEHA sample shows the presence of mesopores, having specific surface area of 280 m^2/g. Additionally, the PVA/PEHA mixed sample has several micropores, having a specific area of 380 m^2/g. Thus, the specific surface area can be increased by adding PVA. The EDLC electrodes were fabricated by using these sample. Fig. 3 shows the current density dependence of capacitance, obtained from charge-discharge measurement within the range of 0 - 1 V. The PVA/PEHA mixed sample exhibits a capacitance of 220 F/g (current density at 50 mA/g) per weight, indicating its higher capacitance than that of the PEHA sample. Consequently, when applied to the electrode material of the capacitor, the specific surface area is larger than the PEHA sample. In addition, the PVA/PEHA mixed sample exhibited a capacitance of 196 F/g at high current density (1000 mA/g) and maintained 89 % of the capacitance at low current density similar to that of the PEHA sample. This result is probably due to the relatively high conductivity of both samples with relatively high crystallinity.
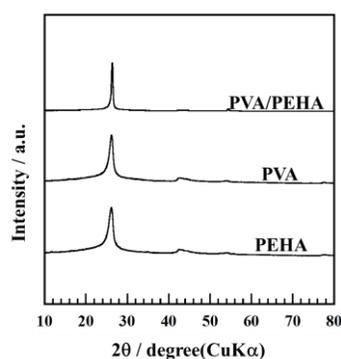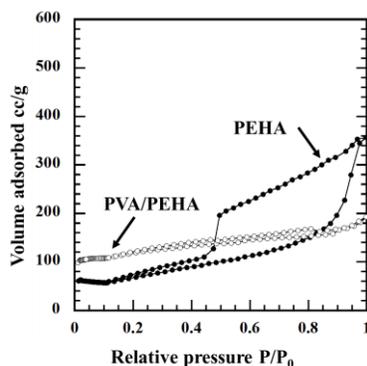

Fig. 1 XRD patterns of the samples.

Fig. 2 N_2 adsorption-desorption isotherms.
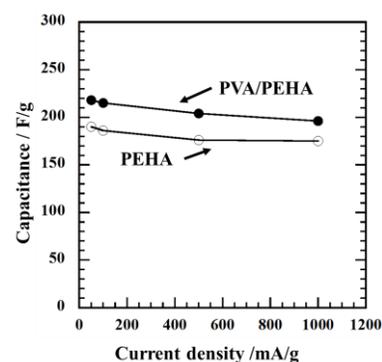

Fig. 3 Current density dependence of electrostatic capacitance.

Conclusions

In this study, carbon materials were prepared through carbonization of polymer compound, and the crystallinity effect and surface properties of the carbon source were investigated. Results indicate that the PVA/PEHA mixed samples have relatively high crystallinity, and the PVA and PEHA sample were also subjected to the effect of $FeCl_3$ catalyst. In addition, PVA/PEHA mixed samples exhibit higher capacitance and superior electrical performance than the PVA and PEHA sample.

References

1. S. Mehare, P. Ranganath, V. Chaturvedi, V. Badiger, (2018) In Situ Synthesis of Nitrogen- and Sulfur-Enriched Hierarchical Porous Carbon for High-Performance Supercapacitor. Energy Fuels, 32, 908 - 915
2. Chieko Abe, Taro Kinumoto, Tomoki Tsumura, Masahiro Toyoda, (2018), Preparation of polyamine-derived nitrogen-doped porous carbon and their evaluation. The 45th tanso zairyo gakkai nenkai, P41
3. G. Sivalingam, G. Madras, Ind. Eng. Chem. Res. (2004), 43, 7716 – 7722,
4. Yasumasa yamazaki, tannso zairyou nyumon, 13 – 27,
5. J. Yuan, C. Giordano, M. Antonietti, Chem. Master. (2010), 22, 5003 – 5012