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研究課題名（和文）Hierarchically-nanostructured carbon particles for energy resource and storage applications

研究課題名（英文）Hierarchically-nanostructured carbon particles for energy resource and storage applications

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研究成果の概要（和文）：本研究では、炭素担持白金（Pt/C）電極触媒の触媒性能に及ぼす種々のカーボンナノ構造の効果を実験的および数値的に評価した。Pt/C触媒は、エアロゾルスプレー熱分解とそれに続くマイクロ波プロセスを用いて調製した。多孔質Pt/C触媒の電気化学的表面積は、中空または緻密なPt/Cのものより2倍以上であった。メソ細孔とマクロ細孔との間のバランスもまた重要であることが見出されている。流体フローモデルは、良好な酸素輸送が触媒活性に寄与していることを示した。さらに、多孔質炭素へのNドーピングの添加は、電極触媒性能をさらに増加させる可能性がある。一方、中空球状炭素の形成は良好なキャパシタンス性能を与えた。

研究成果の概要（英文）：In this study, the effects of various carbon nanostructures on the catalytic performances of carbon supported platinum (Pt/C) electrocatalysts were evaluated experimentally and numerically. The Pt/C catalysts were prepared using a hybrid method involving the preparation of dense, hollow, and porous carbon particle via aerosol spray pyrolysis followed by microwave-assisted Pt deposition. Electrochemical surface area of porous Pt/C catalyst was more than twice than those of hollow or dense Pt/C. The effects of pore size on electrocatalysis were also studied. The results showed the importance of a balance between mesopores and macropores for effective catalysis with a high charge transfer rate. A fluid flow model showed that good oxygen transport contributed to the catalytic activity. Furthermore, the addition of N doping to porous carbon may further increase the electrocatalytic performance. While, the formation of hollow spherical carbon gave a good capacitance performance.

研究分野：　Engineering

キーワード：　Aerosol process　Nanostructured carbon　Energy resources　Energy storages　Polymer

１．研究開始当初の背景

Nanomaterial with an ordered structure may exhibit much higher performance than that of the disordered structure. Morphological control of carbon based catalyst in my previous researches has been proved as an effective strategy to enhance the catalytic performance of proton exchange membrane fuel cell (PEMFC). Well-structured porous carbon particles were successfully prepared by spray pyrolysis of a dual polymer system. Further development of carbon-based particle is crucial for wider application in energy devices.

Structuring strategy is highly desirable yet very challenging to design nanostructured carbon particles because the host carbon NPs are generally hydrophobic in natures, which are not compatible with organic template to make a homogeneous mixture. Hence, it is highly required to find an alternative carbon source.

Development of a self-organized dual polymer system is necessary to address this issue. This research focus on the use of polymer materials as the carbon source and template. To the best of my knowledge, there was no report of designing hierarchically-nanostructured carbon particles from polymers via aerosol route for energy application. Formation mechanisms will be evaluated by investigating the electrostatic forces between the polymers.

２．研究の目的

The purpose of this research is to develop carbon-based materials with controlled morphology for energy applications

(1) Synthesis of nanostructured carbon particles from polymers precursor via aerosol process. Self-organization of two polymers will be carefully evaluated.

(2) Functionalization and catalytic activity measurement of the nano-structured carbon particles by metal deposition and atom doping.

(3) Simulation of the effect of nanostructured morphologies on their hydrodynamic profile.

３．研究の方法

(1) Spray synthesis of nanostructured carbon particles from polymers.

One-step spray pyrolysis consist of a vertical tubular furnace with four controllable temperatures; ultrasonic nebulizer and two-fluid nozzle sprayer as a droplet generator; and electrostatic precipitator as particle collector. To provide an option for scientific and industrial world, polymers which are inexpensive and abundant organic materials was used as the carbon source. Various experimental conditions, such as temperature of furnace, carrier gas flow rate, droplet generator, and polymers type and surface charge were evaluated in detail with respect to its effect to the morphology of final product.

(2) Ultralow Pt loading of carbon-based nanoparticle for catalyst in PEMFC.

Morphology control of carbon as a catalyst support gives high impact to the catalytic performance. However, high amount of Pt loading is still necessary to obtain high catalytic performance. As the preferred solution, this topic will be addressed: (i) improve the electron donor behavior of catalyst by nitrogen (N) doping; (ii) use inexpensive and abundant polymer materials for graphitized-carbon source.

(3) Simulation of the effect of nano-structured morphologies on their hydrodynamic profile.

A computational simulation was conducted to illustrate the theoretical flow pattern of dissolved oxygen inside the catalyst layer during oxygen reduction reaction (ORR) activity tests. The simulation was performed in two steps. The first step was calculation of the electrolyte velocity on the surface of the catalyst layer, using FlexPDE 6.0. In the second step, the velocity distribution inside the catalyst layer was simulated using Autodesk Simulation CFD 2015.

(4) Carbon-based material for capacitive energy storage.

Hollow and porous carbon were synthesized from polymers by controlling the charge of template (i.e. anion or cation). The controlled morphology of electrode ensures electrochemically accessible for ions.

４．研究成果

From the results of 2015-2016 research, the following results and knowledge were obtained

(1) Synthesis of highly dispersed and

controllable size polystyrene latex (PSL) nanoparticles for template application.
Highly dispersed cationic PSL nanoparticles were successfully synthesised via a modified emulsion polymerisation method. Specifically, of 2,2′ -azobis[2-(2-imidazolin-2-yl) propane] di-hydrochloride (VA-044) as the initiator and acetone/water as the solvent medium afforded successful synthesis of cationic PSL particles as small as 31 nm in diameter. The addition of acetone increased the solubility of styrene and reduced the surface tension between the PSL particle surface and aqueous phase. Additionally, rapid diffusion of acetone contributed to the formation of small droplets in the emulsion system, further enabling the formation of PSL nanoparticles. The VA-044 initiator could effectively control the stability of both the surface charge and size of PSL particles.

(2) Synthesis of nanostructured carbon particles from polymers precursor via aerosol process.
Nanostructured hollow and hierarchical porous carbon particles were prepared by spray pyrolysis of a self-organized dual polymer system comprising phenolic resin (as the host material) and charged polystyrene latex (PSL, as the template). The morphology of the prepared particles can be tailored by tuning the attractive or repulsive forces between the precursor components. Strong electrostatic attraction between the phenolic resin and highly positively charged PSL formed hollow carbon particles. Weaker attractive force, as in the case of particles with a small positive charge, or repulsions due to negatively charged PSL, resulted in porous carbon particles. The influence of spray pyrolysis parameters on the carbon morphology, such as temperature of furnace, carrier-gas flow rate, and mass ratio of phenolic resin to PSL, were also investigated thoroughly. It was found that precursor with a mass ratio of phenolic resin to PSL particles of 0.63 produced well-structured porous carbon particles with hexagonally close-packed pores.

(3) Experimental and theoretical approach to evaluation of nanostructured carbon particles.
Correlations to predict the final particle size of dense carbon particles derived from phenolic resin and porous carbon particles derived from phenolic resin and a PSL template, synthesized via spray pyrolysis, have been developed. A residual ratio was introduced as a variable to represent the shrinkage during phenolic resin decomposition. In the porous carbon particle correlation, both residual ratio and porosity were considered in determining the particle size. Using the correlations to predict mean particle diameters showed good agreement with experimental results. The size of dense carbon particles was found to be strongly influenced by the concentration of the phenolic resin. Up to a limiting concentration, the addition of PSL also influenced the size of porous carbon particles. The predicted particle size distributions were narrower than experimental results, possibly due to the segregation and agglomeration of the droplets inside the tubular furnace, but particle size distribution was still well-predicted by the developed correlations.

(4) Electrocatalytic activity of nano-structured Pt/C particles from hybrid aerosol-colloid process.
An optimum nanostructure and pore size of catalyst supports is very important in achieving high catalytic performances. In this instance, the effects of various carbon nanostructures on the catalytic performances of carbon-supported platinum (Pt/C) electrocatalysts were evaluated. The Pt/C catalysts were prepared using a hybrid method involving the preparation of dense, hollow, and porous nanostructured carbon particle via aerosol spray pyrolysis followed by microwave-assisted Pt deposition. Electrochemical characterization of the catalysts showed that the porous Pt/C catalyst gave the best performance; its electrochemical surface area was much higher, more than twice than those of hollow or dense Pt/C. The effects of pore size on electrocatalysis were also studied.

(5) Modelling of morphology-dependent electrocatalytic activity of nano-structured Pt/C particles.
The effects of the catalyst support and pore size on the electrocatalytic performance were studied numerically by fluid dynamic simulations, which were analyzed in terms of electrochemical kinetics. It was found that the performance of the porous carbon Pt/C catalyst was the best among the other morphologies of catalyst, probably because of the presence of interconnected pores, which allowed better oxygen trans-

port to the catalyst surface. Furthermore, good oxygen transport promoted effective charge transfer and consequently increased the active surface area of the catalyst. These results prove the effectiveness of the fluid dynamic approach in qualitatively estimating the electrocatalytic performance by observing hydrodynamic phenomena within the catalyst layer.

(6) Controlled surface topography of particle nanostructures by spray drying process.
The previous results shown in (4) and (5) showed the importance of a balance between meso- and macro-pores for effective catalysis with a high charge transfer rate. Therefore, it is important to successfully prepared well-defined self-organization with coffee-ring-type structures using of carbon source polymer and PSL building block. The complexity of the particle distributions of binary and ternary clusters with different sizes and composition ratios of building block NPs (e.g. PSL, silica, etc.) was discussed. A better understanding of how finite groups of different NPs self-organize in a moving droplet to form a confined geometry may aid in controlling the structure of matter at multiple length scales. Interestingly, the configuration of the large microsphere clusters was found to be influenced by the presence of the small particles, which formed a ring-like structure. This configuration can be used to estimate the balance of carbon pores with various sizes.

(7) Synthesis of nitrogen-functionalized macroporous carbon particles.
In this study, we developed the first synthesis of macroporous carbon particles with high nitrogen content from a melamine resin via spray pyrolysis. A dual-polymer precursor consisting of melamine resin and a PSL template was used to control the carbon particle morphology. The pore size and porous structure were adjusted by changing the PSL particle size and the PSL/melamine resin ratio, respectively. A PSL/melamine resin ratio of 1.6 : 1 gave the best morphology. The nitrogen content of the particles obtained at carbonization temperatures between 600 and 1000 C ranged from 5.44% to 39.2%. The nitrogen content was approximately two to 10 times higher than those achieved using a hydrothermal route.
High-nitrogen content hollow carbon spheres (HCSs) with precisely controllable shell thicknesses (14.2-66.6 nm) and particle size (58.2-320 nm) were also synthesized by a microwave-assisted polymerization and carbonization process from 3-aminophenol as a carbon source and PSL particles as a template. The nitrogen content in the HCSs prepared at 550 C was 15.62%, higher than that in most reported HCSs. We found that shell thickness and particle size could be adjusted by changing the 3-aminophenol/PSL ratio and PSL particle size, respectively. The synthesized HCSs took the advantage of N-doping, indicated by their high capacitive performance (about 17.3% higher than that of commercial activated carbon), long-term cyclic stability, and high energy and power densities.

## ５．主な発表論文等

〔雑誌論文〕（計９件）


① R. Balgis*, L. Gradon, L. Ernawati, T. Ogi, K. Okuyama: Controlled Surface Topography of Particle Nanostructures by Spray Drying Process, AIChE Journal, 査読有, 63 巻, 2017, 1503-1511.
DOI: 10.1002/aic.15682

② L. Ernawati, R. Balgis, T. Ogi, K. Okuyama: Tunable Synthesis of Meso-porous Silica Particle with a Unique Radially Oriented Pore Structures from Tetramethyl Orthosilicate via Oil-Water Emulsion Process, Langmuir, 査読有, 33 巻, 2017, 783-790.
DOI: 10.1021/acs.langmuir.6b04023

③ L. Ernawati, R. Balgis, T. Ogi, K. Okuyama, T. Takada: Role of acetone on the formation of highly dispersed cationic polystyrene nanoparticles, Chemical and Process Engineering Journal, 査読有, 38 巻, 2017, 5-18.
DOI: 10.1515/cpe-2017-0002

④ A. F. Arif, Y. Chikuchi, R. Balgis*, T. Ogi, K. Okuyama: Synthesis of nitrogen-functionalized macroporous carbon particles via spray pyrolysis of melamine-resin, RSC Advances, 査読有, 6 巻, 2016, 83421-83428.
DOI: 10.1039/C6RA15217A

⑤ O. Arutanti, A. F. Arif, R. Balgis*, T. Ogi, F. Iskandar, K. Okuyama: Tailored synthesis of macroporous Pt/$WO_3$ photo-catalyst with nano-aggregates via flame assisted spray pyrolysis, AIChE Journal 査読有, 62 巻, 2016, 3864-3873.
DOI: 10.1002/aic.15349

⑥ A. F. Arif, Y. Kobayashi, R. Balgis, T. Ogi, H. Iwasaki, K. Okuyama: Rapid microwave-assisted synthesis of nitrogen-functionalized hollow carbon spheres with high monodispersity, Carbon, 査読有, 107 巻, 2016, 11-19.
DOI: 10.1016/j.carbon.2016.05.048

⑦ R. Balgis*, A. F. Arif, T. Mori, et al.: Morphology-Dependent Electrocatalytic Activity of Nano-structured Pt/C Particles from Hybrid Aerosol-Colloid Process, AIChE Journal, 査読有, 62 巻, 2016, 440-450.
DOI: 10.1002/aic.15059

⑧ A. F. Arif, R. Balgis*, T. Ogi, T. Mori and K. Okuyama: Experimental and Theoretical Approach to Evaluation of Nanostructured Carbon Particles Derived from Phenolic Resin via Spray Pyrolysis, Chemical Engineering Journal 査読有, 271 巻, 2015, 79-86.
DOI: 10.1016/j.cej.2015.02.078

⑨ R. Balgis*, T. Ogi, A. F. Arif, et al.: Morphology control of hierarchical porous carbon particles from phenolic resin and polystyrene latex template via aerosol process, Carbon, 査読有, 84 巻, 2015, 281-289.
DOI: 10.1016/j.carbon.2014.12.010

〔学会発表〕(計 11 件)
① R. Balgis, A. F. Arif, T. Ogi, K. Okuyama: Effect of nanostructured Pt/C particles morphologies on electrocatalytic activity, 化学工学会第 82 年会(2017,3,8 芝浦工業大学)
② R. Balgis: [The SCEJ Award for Outstanding Young Researcher] Spray Route to Synthesize Nanostructured Carbon Particle for Energy and Environmental Application, 化学工学会第 82 年会(2017,3,8 芝浦工業大学)
③ R. Balgis: Synthesis of Nano-structured Particles via Spray Process for Energy Application, Guest Lecture at Department of Chemical Engineering (2017,3,31 スラバヤ工科大学(ITS), Indonesia)
④ 築地 陽平, R. Balgis, 荻 崇, 奥山 喜久夫: 噴霧熱分解法によるポーラス窒化炭素微粒子の合成, 化学工学会 第 48 回秋季大会 (2016,9,6 徳島大学)
⑤ R. Balgis, T. Mori, et al.: Hierarchical Porous Carbon Particles Prepared via Spray Pyrolysis of Phenolic Resin and PSL, 化学工学会第 81 年会(2016,3,14 関西大学)
⑥ R. Balgis: Synthesis of Nanostructured Carbon Particles via Aerosol Process for Energy & Environmental Application, Guest Lecture at Dept. of Environmental Engineering (2015,12,22 Tsinghua University, Beijing, China)
⑦ R. Balgis: Aerosol Synthesis of Hierarchical Nanostructured Carbon Particles using a Dual Polymer System, The 6th Nanoscience and Nano-technology Symposium (NNS 2015), (2015,11,5 The Sunan Hotel Solo, Indonesia) Invited Speaker
⑧ R. Balgis, K. Okuyama: Aerosol Syn-thesis of Nanostructured Carbon Particles from Dual Polymer System, European Aerosol Conference (EAC 2015), (2015,9,5-11 Milan, Italia)
⑨ R. Balgis: Nanoparticles Dispersion and Nanostructurization for Energy and Environmental Applications, Guest Lecture at Dept. of Mechanical and Nuclear Engineering (2015,7,18 Virginia Commonwealth University (VCU), Virginia, USA)
⑩ R. Balgis, T. Ogi, K. Okuyama: Aerosol Synthesis of Self-Organized Nanostructured Carbon Particles from Polymers, Asian Aerosol Conference (AAC2015), (2015,6,24-26 Kanazawa)
⑪ R. Balgis, T. Mori, T. Ogi, et al.: Self-Organized Macroporous Carbon Particle from Phenolic Resin via Spray Pyrolysis for catalyst application, Japan Powder Technology Spring Meeting, (2015,5,19-20 Tokyo)

〔図書〕(計 0 件)
None

〔産業財産権〕
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None

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None

〔その他〕
ホームページ等
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