Technology

Porous Carbon Material “ESCARBON™ MCND” for Catalyst Support of Polymer Electrolyte Fuel Cells

Kazuyoshi MASAKI*
Kenichiro TADOKORO
Noboru DAITO
Mitsuru KOHNO
Takashi IIJIMA
Masataka HIYOSHI

Abstract

Nippon Steel Chemical & Material Co., Ltd. has successfully commercialized a newly developed mesoporous carbon material, ESCARBON™ MCND, manufactured using a custom-designed synthesis process and technology. The precursor of MCND is silver acetylide (Ag_2C_2), and the resulting carbon exhibits a dendritic structure with internal pores partitioned by layers of graphene sheets. The primary pore size is on the order of several nanometers. As a result of its unique mesoporous architecture, MCND significantly enhances the catalytic activity of Polymer Electrolyte Fuel Cells (PEFCs). Furthermore, its structure-composed of multiple graphene layers-provides excellent oxidation resistance, contributing to improved catalyst durability.

1. Introduction

Polymer Electrolyte Fuel Cells (PEFCs) have garnered significant attention as clean and highly efficient power generation systems. A critical component of PEFCs is platinum, which functions as the catalyst. However, due to the high cost of platinum, considerable efforts have been made to reduce its usage by micronizing platinum particles to sizes in the range of 2–5 nm. This strategy increases the catalytic surface area, thereby enhancing activity per unit weight.[1)]

To stabilize these micronized platinum particles and prevent agglomeration, carbon supports with high specific surface areas are commonly employed. In addition to offering a large surface area, the carbon support must possess macropores to facilitate the diffusion of gases and water, as well as exhibit excellent electrical conductivity and oxidation resistance.[2)]

This paper introduces a novel carbon support material-Mesoporous Carbon Nano Dendrites (MCND), commercially known as ESCARBON™ MCND. This advanced material has been adopted in fuel cell vehicles due to its superior performance as a support for platinum catalysts.

2. ESCARBON™ MCND

MCND is a porous carbon material with a unique structure, synthesized from silver acetylide as its precursor. Owing to its distinctive architecture, MCND has been adopted in fuel cell vehicles as a catalyst support. Even with a reduced amount of catalyst metal compared to conventional carbon materials, MCND enables high power generation performance. Furthermore, its structure—composed of multiple graphene layers—provides practical oxidation resistance. These features have contributed significantly to the reduction of platinum catalyst usage and the downsizing of fuel cell systems.[3)]

2.1 MCND preparation procedure

The basic procedure for preparing MCND has been described by Nishi et al.[4, 5)] When acetylene is introduced into an ammonia solution containing silver nitrate, a white precipitate of Ag_2C_2 is formed. The precipitated Ag_2C_2 exhibits a dendritic structure composed of branches approximately 50 nm in diameter, which develop into complex branched networks, resulting in the formation of numerous pores (**Fig. 1**). The obtained Ag_2C_2 is thoroughly washed to remove the by-product ammonium nitrate, and the wet Ag_2C_2 material is placed in a vacuum chamber. After degassing and drying, the vacuum chamber is heated to temperatures above 150°C. This thermal treatment triggers a phase transition of Ag_2C_2 ($Ag_2C_2 \rightarrow 2C + 2Ag$), resulting in a black powder composed of a mixture of silver and carbon. The silver component in the mixture can be removed using a conventional method, such as washing with nitric acid. After the removal of silver, the material undergoes heat treatment to adjust its

* Senior Researcher, New Materials Development Center, Research & Development Div., Nippon Steel Chemical & Material Co., Ltd.
46-80 Oaza Nakabaru Sakinohama, Tobata-ku, Kitakyushu City, Fukuoka Pref. 804-8503

crystallinity, which optimizes the material's properties-specifically electrical conductivity and oxidation resistance-required for fuel cell support applications. Through this sequence of processes, a porous carbon material referred to as MCND is obtained.

2.2 Structure of MCND

To investigate the pore structure of mesoporous carbon nanodendrites (MCND), nitrogen adsorption measurements and pore size distribution analysis via mercury intrusion porosimetry were conducted. **Table 1** summarizes the representative physical properties of MCND.

The Brunauer-Emmett-Teller (BET) specific surface area of MCND is remarkably high at 1 200 m^2/g, demonstrating its potential effectiveness as a catalyst support. Similarly, the mesopore volume reaches 0.9 mL/g, underscoring the material's extensive porous architecture. Pore size distribution analysis using the Dollimore-Heal (DH) method reveals that the mesopores predominantly range from 2 to 10 nm (**Fig. 2**). Mercury intrusion porosimetry further indicates the presence of numerous macropores within the 20 to 100 nm range (**Fig. 3**).

Scanning electron microscopy (SEM) images of heat-treated MCND (**Fig. 4**) demonstrate that the dendritic morphology derived from silver acetylide is preserved following phase transfer and thermal treatment. Large macropores are observed between the dendritic branches, facilitating the transport of gases and water (Fig. 4a). These macropores correspond to the 20–100 nm pores identified via mercury intrusion. Furthermore, the particle surfaces display complex topographical features, such as elevations and depressions, some of which may contain openings formed by the ejection of silver during the phase transfer process (Fig. 4b).

Transmission electron microscopy (TEM) images (**Fig. 5**) reveal that the branches of MCND contain a multitude of internal pores enclosed by several layers of graphene sheets. These internal pores, ranging from 2 to 10 nm, are consistent with the mesopore distribution shown in Fig. 2 and contribute significantly to the high specific surface area and mesopore volume. It is also inferred that these internal pores are interconnected and may be linked to the external surface through openings created during silver ejection.

In conclusion, MCND exhibits a hierarchical porous structure comprising interconnected mesopores within the dendritic branches, robust walls formed by graphitic layers with high oxidation resistance, and large macropores between branches that facilitate gas dif-

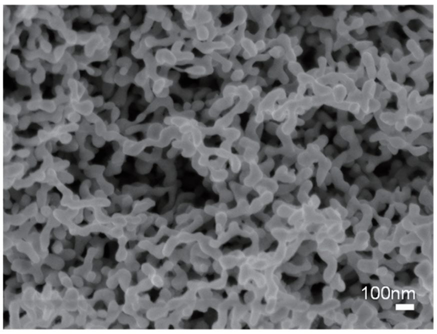


Fig. 1 SEM image of an Ag_2C_2 dendrite monolith

Table 1 Pore characteristics of MCND

BET surface area (m^2/g)	Micro pore volume (mL/g)	Meso pore volume (mL/g)
1 200	0.2	0.9

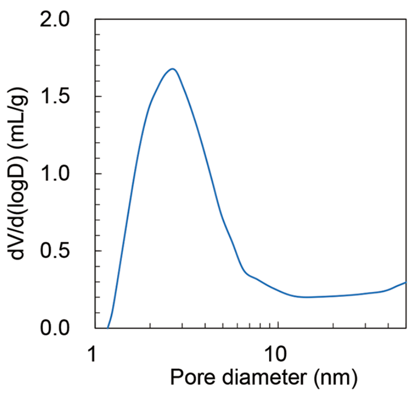


Fig. 2 Pore size distribution (determined by the DH analysis of nitrogen adsorption isotherms)

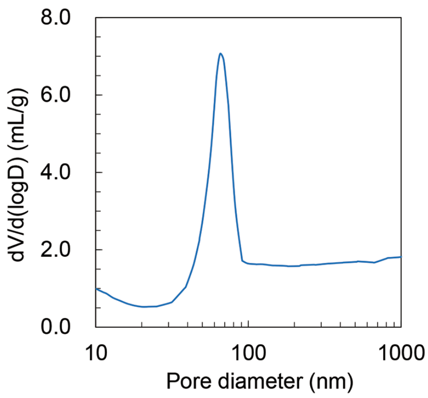


Fig. 3 Pore size distribution on the mercury intrusion porosimetry

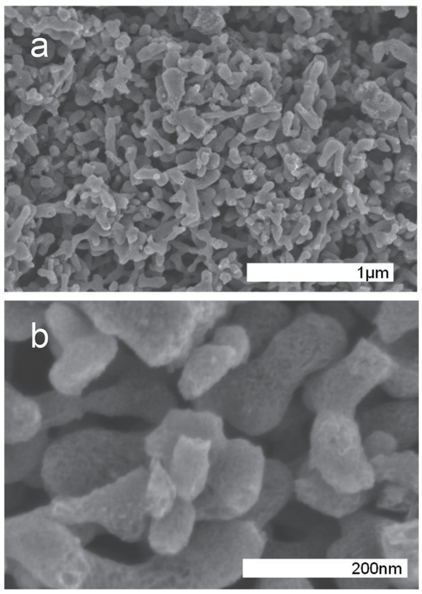


Fig. 4 SEM images of MCND

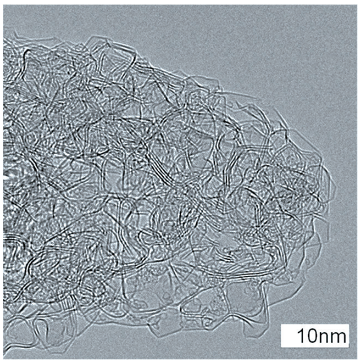


Fig. 5 TEM image of MCND

fusion. These structural features make MCND a promising candidate for use as a support material in fuel cell applications.

3. MCND as Fuel Cell Support

In this study, we synthesized a platinum catalyst supported on MCND (Pt/MCND) and, for comparison, a platinum catalyst supported on solid carbon black (Niteron #SH, manufactured by Nippon Steel Chemical & Material Co., Ltd.), used as a conventional Pt/CB. The power generation performance of these catalysts in fuel cell applications was evaluated, as shown in **Fig. 6**.

At low current densities, where fuel gas consumption is limited and mass transport effects are minimal, the cell voltage is primarily influenced by the intrinsic catalytic activity. In contrast, at high current densities, where fuel consumption increases and significant water generation occurs, gas diffusivity becomes a critical factor.

Across the entire current density range, Pt/MCND exhibited superior performance compared to Pt/CB. This indicates that MCND offers enhanced catalytic activity as well as improved gas diffusivity.

Figure 7 presents SEM and STEM images of the Pt/MCND catalyst. In the SEM image, platinum particles appear as white spots, while in the STEM image, they are observed as black spots. The SEM image primarily reveals particles located on the outer surface, whereas the STEM image captures both surface and internal particles. These observations suggest that a significant portion of the platinum nanoparticles are embedded within the MCND structure.

Figure 8 illustrates the mechanism by which MCND enhances catalytic activity. In conventional carbon-supported catalysts, platinum particles on the outer surface can be covered by ionomer (polymer electrolyte), which may limit their catalytic activity.[6, 7] In contrast, platinum particles located inside the porous MCND structure are less affected by ionomer coverage, as the ionomer cannot easily penetrate the internal pores. Consequently, the catalytic activity of these internal particles is preserved, contributing to the overall enhancement in performance observed with Pt/MCND.

4. Conclusion

Nippon Steel Chemical & Material has successfully commercialized a newly developed mesoporous carbon material, ESCARBON™ MCND, manufactured using a custom-designed synthesis process and technology. This paper introduced the structural characteristics and functional advantages of ESCARBON™ MCND. Owing to its unique pore architecture, MCND has been adopted in commercially available fuel cell vehicles (FCVs), contributing to the advancement of a hydrogen-based society through the widespread deployment of FCVs. Looking ahead, MCND is expected to find applications in a broader range of fields beyond fuel cells.

References

1) Minhua, S. et al.: Nano Lett. 11 (9), 3714 (2011)
2) Shioyama, H. et al.: Tanso. 2003 (210), 236 (2003)
3) Mizuno, S. et al.: Toyota Technical Review. 66, (2021)

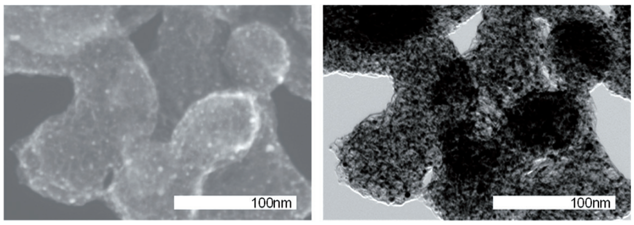


Fig. 7 SEM (left) image and STEM (right) image of Pt/MCND

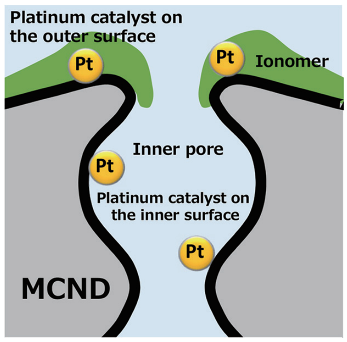
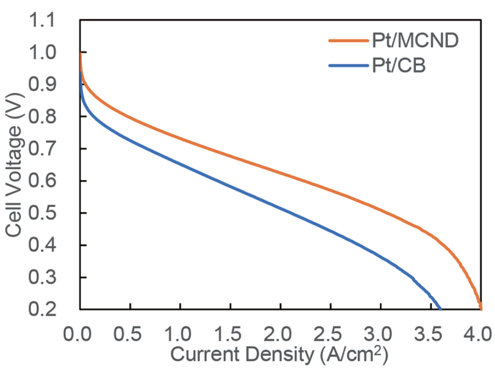


Fig. 8 Influence of ionomer covering depending on catalyst position



	Pt/MCND	Pt/CB
Pt loading (mass%)	40	30
Ionomer / Support(mass ratio)	0.63	0.45
Pt amount(mg/cm^2)	0.2	0.2

Cell temperature : 80(°C)
RH : Anode/Cathode = 100/100(%)
Pressure : Anode/Cathode =100/100(kPaG)
Gas : Anode/Cathode = H_2/Air
Gas flow rate : Anode/Cathode = 0.5/1.0(NL/min)

Fig. 6 Cell performances of Pt/MCND and Pt/CB

4) Japanese Patent Announcement. Patent No. 5481748. April 23, 2014
5) Numao, S. et al.: Carbon. 47 (1), 306 (2009)
6) Ohma, A. et al.: Electrochim. Acta. 55 (28), 8829 (2010)
7) Shinozaki, K.: J. Power Sources. 325, 745 (2016)

Kazuyoshi MASAKI
Senior Researcher
New Materials Development Center
Research & Development Div.
Nippon Steel Chemical & Material Co., Ltd.
46-80 Oaza Nakabaru Sakinohama, Tobata-ku,
Kitakyushu City, Fukuoka Pref. 804-8503

Mitsuru KOHNO
Ph.D., Head of Center
New Materials Development Center
Research & Development Div.
Nippon Steel Chemical & Material Co., Ltd.

Kenichiro TADOKORO
Chief Researcher
New Materials Development Center
Research & Development Div.
Nippon Steel Chemical & Material Co., Ltd.

Takashi IIJIMA
Ph.D., Principal Researcher
Advanced Technology Research Laboratories
Nippon Steel Corporation

Noboru DAITO
Group Leader
New Materials Development Center
Research & Development Div.
Nippon Steel Chemical & Material Co., Ltd.

Masataka HIYOSHI
Senior Researcher
Composite Materials Research Dept.
New Materials Research Lab.
Advanced Technology Research Laboratories
Nippon Steel Corporation