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研究課題名（和文）Doped Graphene Foam as a Model Oxygen Reduction Reaction Electrocatalyst System

研究課題名（英文）Doped Graphene Foam as a Model Oxygen Reduction Reaction Electrocatalyst System

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研究成果の概要（和文）：窒素ドープカーボンフォームを調製し、Ptフリー電極触媒の酸素還元反応のためのモデルシステムとして用いた。メタルフリー窒素ドープカーボンフォームを合成後、このカーボンフォームに鉄を含浸させたものと物性比較を行った。酸性溶媒中のFe-N-C触媒は、大きなポアによる拡散性の高さから市販のPtフリー触媒よりも優れた性能を示したが、Pt / Cには劣った。アルカリ性溶媒中のFe-N-C触媒は、Pt/Cを上回る性能を示した。活性部位での反応メカニズムを明らかにした。また耐久性評価の結果からアルカリ性溶媒中でのPtフリー触媒の優れた安定性が明らかとなり、劣化メカニズム解明を透過電子顕微鏡観察を用いて行った。

研究成果の概要（英文）：Template-free nitrogen-doped carbon foams with large surface area are used as a model system to study the oxygen reduction reaction in Pt-free electrocatalysts. Metal-free nitrogen doped carbon foams are synthesized and compared with iron-impregnated nitrogen-doped carbon foams. In acid medium the resulting Fe-N-C catalysts out-perform commercially available Pt-free catalysts due to excellent mass diffusion through the relatively large pores, but still do not compete with Pt/C. In alkaline medium the Fe-N-C catalysts out-perform both commercial Pt-free catalyst and Pt/C. Detailed materials characterization is performed to lend insight into the possible nature of the active sites. Detailed durability studies reveal the excellent stability of Pt-free catalysts in alkaline medium and post-durability transmission electron microscopy is used to investigate the degradation mechanisms.

研究分野：　Electrochemistry

キーワード：　Electrochemistry　Catalysis　Nitrogen-doped carbon　Oxygen reduction　non-precious　Pt-free　Fe-N-C　Fuel Cells

１．研究開始当初の背景

The platinum cathode catalyst contributes significantly to the high cost of PEFCs. Research into alternative Pt-free catalysts for the oxygen reduction reaction (ORR) has been underway for decades. The most promising non-precious catalysts are transition metal-containing nitrogen-doped carbon materials, generally synthesized by pyrolysis of various mixtures of iron, nitrogen, and carbon precursors. It is well established that the final performance of such catalysts is dependent on a wide variety of different factors, including the proportions and ratios of the different elements, the chemical configuration of these elements, and in particular, the chemical environment of nitrogen and transition metal species in the carbon matrix. In addition, other factors such as conductivity and microstructure play an important role. All of the above factors can vary wildly depending on the type and ratio of precursors used, the pyrolysis temperature, the rate of heating during pyrolysis, the gases used in pyrolysis, and the type of support used, if any.

Understanding the exact nature of the active sites for the ORR is of paramount importance in order to realize the implementation of efficient and affordable fuel cells. However, despite decades of research we are still some way from pinning down the exact mechanism, and controversy still dominates the field. These materials have complex and non-uniform chemical structures incorporating Fe, N, C (and also O), all of which can bond to each other in multiple and unpredictable configurations. Broadly speaking, there are three main theories on the nature of the active site. The first is that some configuration of nitrogen-doped carbon can catalyze 4-electron ORR. The second and most popular theory attributes the ORR to atomically-dispersed porphyrin-like Fe-N-C moieties. The third and most recent mainstream theory considers carbon-encapsulated superparamagnetic Fe nanoparticles as the active sites for the ORR.

２．研究の目的

To develop and optimize a nitrogen-doped carbon foam-based support for Pt-free Fe-N-C electrocatalysts. To compare the ORR activity of Fe-free nitrogen-doped carbons and Fe-decorated nitrogen-doped carbons in order to explore the ORR mechanism in detail in both acid and alkaline media. To shed light on what conditions are needed for 4-electron ORR to occur, namely which elements in which atomic configuration are required. To investigate the durability of these Fe-N-C catalysts for the ORR in both acid and alkaline media. Eventually to synthesize improved Pt-free electrocatalysts based on the above findings.

３．研究の方法

Nitrogen-doped carbon foams were prepared by reacting sodium with TEA, anhydrous ethanol, in THF solvent to form a nitrogen-containing alkoxide product. This was pyrolysed, and washed to form samples labelled N-C. To make Fe-containing catalysts, a dispersion of the N-C was mixed with iron acetate (FeAc), before a second pyrolysis step to produce samples labelled Fe-N-C. Materials were characterized by BET surface area analysis; BJH pore size distribution analysis; X-ray Diffraction (XRD); scanning electron microscopy (FE-SEM); transmission electron microscopy (TEM; and X-ray photoelectron spectroscopy (XPS); linear sweep voltammetry (LSV), cyclic voltammetry (CV).

４．研究成果

The synthesis of template-free nitrogen-doped carbon foams was successfully performed. The microstructure was investigated by SEM, revealing a macroporous material with micron-scale pores separated by very thin carbon walls (Fig. 1).

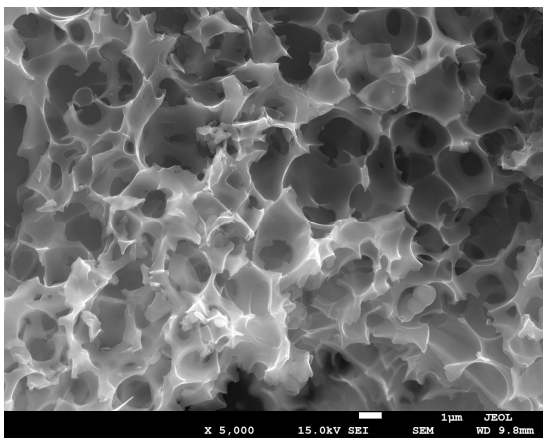

Figure 1: SEM image of a typical nitrogen-doped carbon foam sample.

TEM confirms the extrmely thin nature of the carbon walls (Fig. 2). After Fe impregnation and pyrolysis, iron nanoparticles encapsulated by graphitic carbon are observed to be decorated on the nitrogen-doped carbon support.

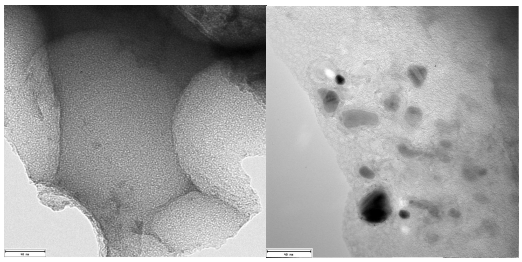

Figure 2. TEM images of N-C and Fe-N-C electrocatalysts. Scale bar is 40 nm.

By modifying the precursor ratios and pyrolysis conditions, the nitrogen content and microstructure of the N-C carbons was optimized. The surface area was increased to 2500 m^2/g by using suitable synthesis conditions (Figure 3).

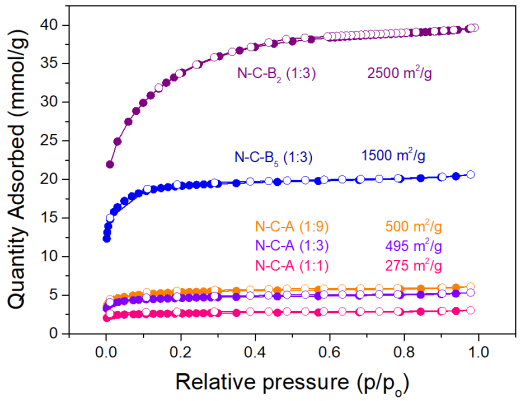

Figure 3: Nitrogen adsorption isotherms and surface area of nitrogen-doped carbon foams synthesized by different protocols.

The electrochemical activity was investigated first in acid medium (Fig. 4). By using the optimized nitrogen-doped carbon foam supports impregnated with iron, electrocatalysts were produced with higher ORR activity than equivalent commercially available electrocatalysts (NPC-2000). This improvement in activity is attributed to a high density of active sites afforded by the unique microstructure of the material, as well as efficient mass diffusion through the relatively large pores.

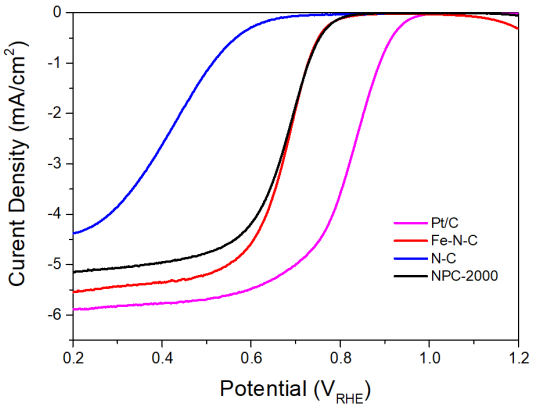

Figure 4. LSVs of Fe-free and Fe-impregnated nitrogen-doped carbon foams compared with a commercial Fe-N-C catalyst (NPC-2000) and Pt/C in acid.

In alkaline medium the ORR activity is much improved (Fig. 5). In this case the activity of the Pt-free catalysts is much higher than in acid media, due to the faster kinetics at high pH. In this case, the Fe-impregnated nitrogen-doped carbon foam out-performs both the commercial Pt-free catalyst as well as Pt/C. This shows that by taking care to optimize the carbon support microstructure and pyrolysis conditions, as well as understanding the formation of active site, superior electrocatalysts can be synthesized.

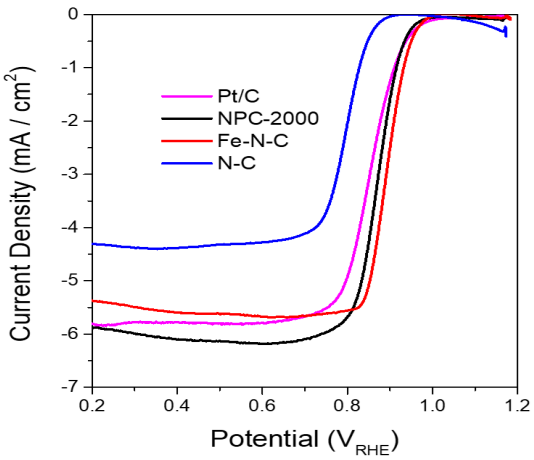

Figure 5. LSVs of Fe-free and Fe-impregnated nitrogen-doped carbon foams compared with a commercial Fe-N-C catalyst (NPC-2000) and Pt/C in alkaline.

The electrochemical durability in alkaline medium was investigated over 60,000 load potential cycles (Fig. 6). It was found that Fe-free catalysts are extremely stable, but have lower ORR activity. Fe-containing catalysts with atomically dispersed Fe (i.e.

NPC-2000) have excellent stability, whilst in samples rich in Fe nanoparticles (i.e. Fe-N-C) the performance degrades significantly. This lends particular insight into the nature of the active sites in these different materials.

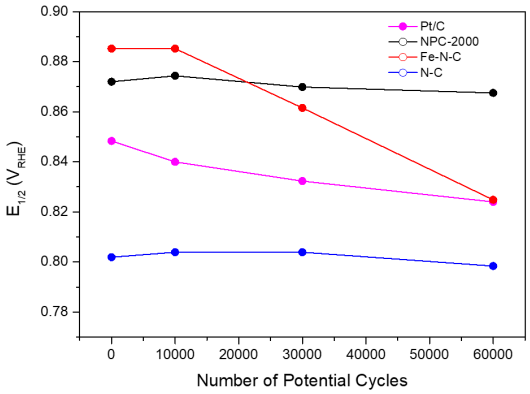

Figure 6. Electrochemical durability in alkaline medium.

Further work is underway to investigate these samples using X-ray adsorption spectra, in combination with density functional theory calculations to gain more insight into the exact nature of the ORR active site.

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〔産業財産権〕

○出願状況（計 0 件）

名称：
発明者：
権利者：
種類：
番号：
出願年月日：
国内外の別：

○取得状況（計　　件）

名称：
発明者：
権利者：
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番号：
出願年月日：
国内外の別：

〔その他〕
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https://sites.google.com/site/graphenegnome/

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