HT-XAFS for Elucidating the Formation Mechanisms of ORR Active Sites in Fe-N-C Electrocatalysts

A. Mufundirwa,1 K. Ogi,2 S. Yoshioka,2,6 T. Sugiyama,6 G. F. Harrington,7,9 K. Sasaki,1,5,7 A. Hayashi,1,8 S. M. Lyth5,8,10*

1Department of Mechanical Engineering; 2Department of Applied Quantum Physics and Nuclear Engineering, 6Research Centre for Synchrotron Light Applications (RCSLA); 8Platform of Inter/Transdisciplinary Energy Research (Q-PIT), Kyushu University.

Iron-decorated nitrogen-doped carbon (Fe-N-C) catalysts could replace platinum in fuel cells. However, there is lack of understanding of the formation mechanisms of active sites in these materials. Here, we utilise a nitrogen-doped carbon foam support with optimised porosity, surface area, and conductivity. This is infiltrated with iron (II) acetate and heat treated, changing the chemical state of the adsorbed iron, whilst the support properties are relatively unchanged. High temperature X-ray adsorption spectroscopy (XAS) was used to observe changes in the adsorbed iron in-situ during synthesis, revealing the transition from Fe-O bonds in FeAc at low temperature to Fe-N bonds at 700 °C as the iron binds with nitrogen atoms in the support. At 900 °C Fe-Fe bonds are observed as the iron is reduced to metal, forming carbon-encapsulated nanoparticles. These physical changes significantly affect the electrochemical activity.

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A. Mufundirwa,[1] K. Ogi,[2] B. Smid,[3] B. V. Cunning,[4] Y. Shundo,[5] S. Yoshioka, [2,6] T. Sugiyama,[6] G. F. Harrington,[7,9] K. Sasaki,[1,5,7] A. Hayashi,[1,8] S. M. Lyth[5,8,10*]

[1]Department of Mechanical Engineering, Kyushu University; [2]Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University,
[3]Charles University, Prague, Czech Republic, [4]UNIST, Ulsan, Republic of Korea, [5]International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University
[6] Research Centre for Synchrotron Light Applications (RCSLA), Saga Light Source, Kyushu University Beamline BL06, Saga Light Source, Tosu, Japan,
[7]Next-Generation Fuel Cell Research for Hydrogen Energy, Kyushu University, [8]Platform of Inter/Transdisciplinary Energy Research (Q-PIT), Kyushu University,
[9]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA., [10]Energy 2050, University of Sheffield, UK

KYUSHU UNIVERSITY

NEXT-FC Next-Generation Fuel Cell Research Center

Introduction

❖ 固体高分子形燃料電池(PEFCs)はカーボンに分散担持された白金触媒(Pt/C)が用いられ，高効率のグリーンエネルギー変換デバイスとして知られている.

❖燃料電池の商業化は，白金がハイコストであることに起因し，促進されていない.

❖炭素ベースのカソード触媒(Fe-N-C)は優れた酸素還元反応(ORR)を示す.

❖現在，いくつかの企業(Pajarito Powder, Ballard, 日清紡，ダイハツ)はFe-N-Cの研究を行っている.

❖しかし，Fe-N-Cの活性部位はあまり理解されておらず，広く普及されていないのが現状である

❖本研究では **Fe-N-Cの活性部位の解明を目的とし，"de-coupling"アプローチを利用し，初めにベースを作製し，次に鉄を担持した.**

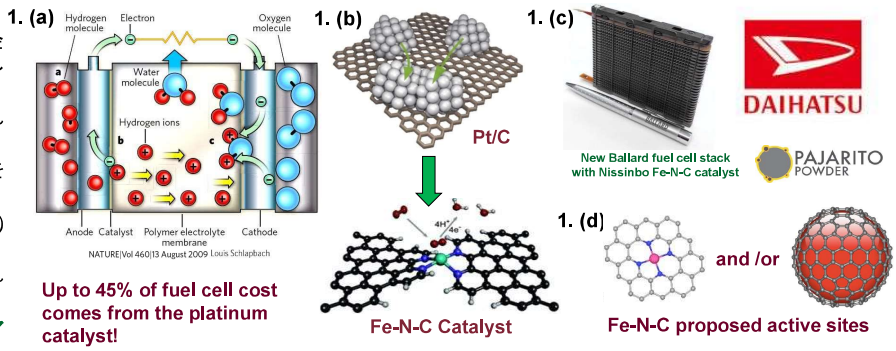


Figure 1: (a) PEFC schematic, (b) Pt/C to Fe-N-C schematic (c) Commercial Fe-N-C systems (d) Proposed active sites

Support Synthesis

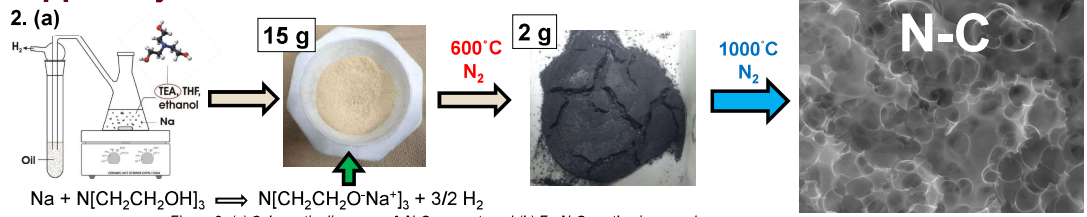


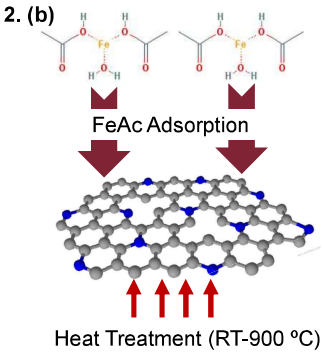
Figure 2: (a) Schematic diagrams of N-C support, and (b) Fe-N-C synthesis procedures.

❖ナトリウム，トリエタノールアミン(TEA)，エタノールおよび溶媒を撹拌し，ロータリーエバポレーターで蒸発させ，箱型の炉で熱分解をした.その後，純水でNaOHを除去した.

❖1000˚Cで2時間，2回目の熱分解を行い，N-Cを形成した.

❖N-Cと酢酸鉄(FeAc)は撹拌，ろ過，乾燥させ，150˚C・300˚C・500˚C・700˚C・900˚Cでそれぞれ2時間，アンモニア(NH_3/N_2)の熱処理を行った.

Iron-Decoration



Results

1. BET and XRD

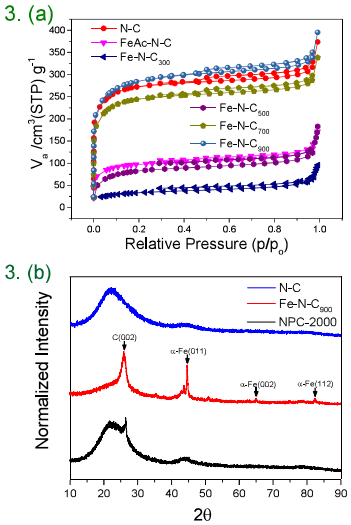


Figure 3: (a) BET of N-C and Fe-N-C samples, and (b) XRD of N-C, Fe-N-Cs and commercial Fe-N-C sample.

2. XPS and EXAFS

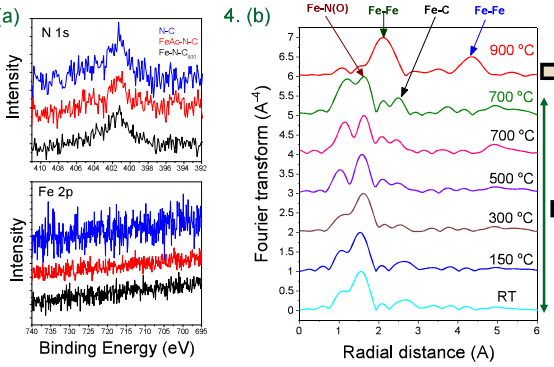


Figure 4: (a) N 1s and Fe 2p XPS, and (b) EXAFS

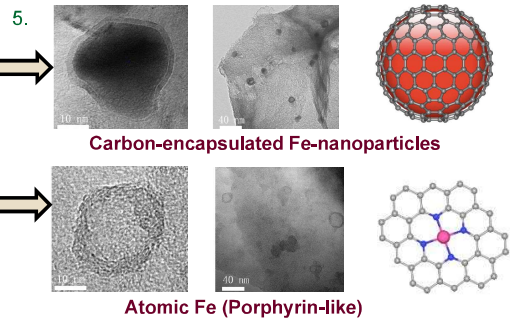
❖ XPSからFeAcの添加は原子濃度にほとんど影響を与えず，N-Cの安定性を示す.

❖FeAcは150~300˚Cの間で分解される.

❖Fe-Nの結合は300~700˚Cの範囲で形成される.

❖700˚C以上ではFe-Nの結合が分解され，炭素カプセル化された鉄のナノ粒子が形成される.

3. Transmission electron microscopy



❖N-CとFe-N-CはI型のマイクロポアを有する.

❖FeAcを担持した触媒は表面積の減少時に観察され，微細孔が塞がれたを示唆した.

❖しかし，Fe-N-C_{700}およびFe-N-C_{900} はN-Cと同様な等温線を示し，FeAcの添加は多孔性にほとんど影響を与えなかった.

❖XRDからFe-N-C_{900}はN-Cおよび市販のFe-N-Cと比べて，優れた黒鉛化によりピークが顕著に示された.

4. Electrochemical Characterization

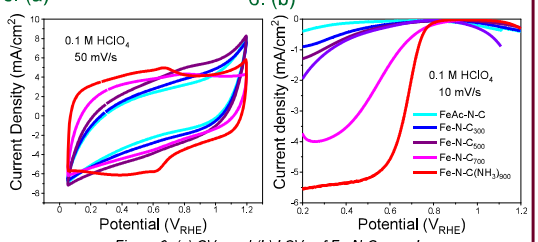


Figure 6: (a) CVs and (b) LSVs of Fe-N-C samples

❖500˚C以下で加熱されたFe-N-CはほとんどORR活性を示さなかった.

❖触媒活性は700˚C以上で大幅に改善された.

Conclusions

❖高表面積 (1600 m^2/g) を有する窒素ドープカーボン(N-C)は安価な前駆体で合成され，ORRにおける非PGM触媒として評価された.

❖低温での熱分解は主にORR活性を示し，700˚C以上での熱分解はFe-N結合におけるORR活性および炭素カプセル化されたFeナノ粒子の形成が示された.

❖**今後の展望:** 最適化，耐久性，NAP-XPS, Mössbauer. In-Situ XAFS, HR-TEM, FIB-SEM, Fe-N-CベースのMEA製造

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