

### Electrochemical Oxygen Reduction on Metal-Free Nitrogen-Doped Graphene Foam in Acidic Media

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Polymer electrolyte membrane fuel cells (PEMFCs) are set to revolutionize the energy industry. Commercial PEMFC stationary units for industrial / home use have been on sale for the past few years in Japan, and PEMFC vehicles will be commercialized in 2015. However, due to the use of Pt in current technology, PEMFCs are currently expensive and have limited durability.

Non-precious, Pt-free catalysts for the electrochemical oxygen reduction reaction (ORR) in acid media have been the subject of intense research for the past few decades. One of the key classes of materials in this promising field are pyrolysed mixtures of Fe/C/N-containing precursors, subjected to various recipes of heating, acid washing, and milling. The mechanism for the ORR in these non-precious catalysts is not well understood, and is still heavily debated. There are two main camps; those who see Fe as a key element in the catalytic center, and those who believe Fe creates active sites, but plays no active catalytic role in the ORR. The history of this field is well-summarized in a recent review.<sup>1</sup>

We added a little clarity to the debate by synthesizing metal-free carbon nitride. We performed electrochemical tests on this material and found some inherent catalytic activity, limited by poor electronic conduction and surface area.<sup>2</sup> Next we supported carbon nitride on carbon black / carbon nanotubes and subjected it to high temperature treatment to increase the electronic conductivity / surface area.<sup>3,4</sup> Finally, we synthesized and tested a metal-free nitrogen-doped (N-doped) graphene foam.<sup>5</sup> It was concluded that although high current densities such as those seen in Fe-containing samples were not achieved, some 4-electron ORR transfer was observed in systems containing only carbon and nitrogen.

Here, we synthesis an N-doped graphene foam from cheap and simple precursors (sodium and diethanolamine). These are reacted together to form a nitrogen-containing alkoxide which is then combusted to form a black powder. This is washed, heat treated variously in N<sub>2</sub> and H<sub>2</sub> at up to 1500°C, and milled.

The resulting material is a graphene foam with a cell size of the order 2 μm, and with thin graphene walls (Figure 1). The maximum surface area measured by BET is 1180 m<sup>2</sup>/g. Taking into account the theoretical maximum surface area of graphene (2630 m<sup>2</sup>/g), this corresponds to an average thickness of ~2.2 graphene layers.

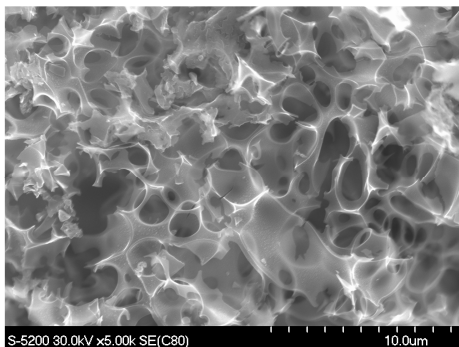


Figure 1. SEM image of N-doped graphene foam.

Raman spectroscopy shows well-defined G, D and 2D peaks. The D peak is large relative to the G peak, showing that this graphene is quite defective. This may be due to the relatively low temperature / catalyst free synthesis, or the presence of nitrogen. The 2D peak at ~2700 cm<sup>-1</sup> is indicative of graphene. X-ray photoelectron spectroscopy (XPS) reveals a nitrogen content of 2.9 at.%, containing pyridinic, quaternary, pyrrol and amine functional groups.

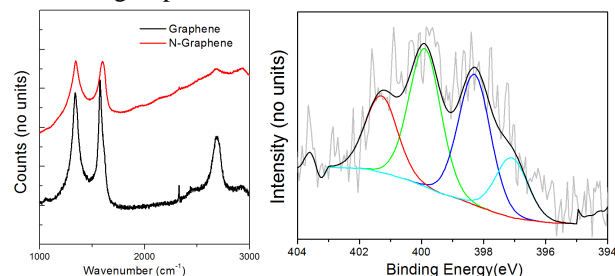


Figure 2. (a) XPS and (b) Raman spectroscopy.

Figure 3 shows linear sweep voltammograms (LSVs) of the N-doped graphene foam, compared with earlier samples. The current density has been almost doubled by optimizing the synthesis steps. The onset potential (the voltage at which current density is first detected) is ~0.85 V, which is similar to that of many Fe-containing catalysts. The number of electrons was estimated from the proportion of H<sub>2</sub>O<sub>2</sub> detected at a rotating platinum disk. The resulting value, ~3 electrons, suggests that an approximate equal mix of 2- and 4-electron transfer is occurring. This is in agreement with our previous work on Fe-free nitrogen-doped carbons. Which precise combination of carbon and nitrogen atoms is still not clear, and determining this will be the subject of future studies.

We conclude from this that Fe-free active sites may contribute significantly to the ORR in Fe/C/N-based catalysts. The role of Fe is still not clarified. It may contribute directly to 4-electron ORR; it may help generate a large excess of 4-electron carbon-nitrogen sites; it may suppress formation/activation of 2-electron carbon-nitrogen active sites; or it may be a combination of these factors. Whichever of these mechanisms is correct, more work needs to be done in this exciting field.

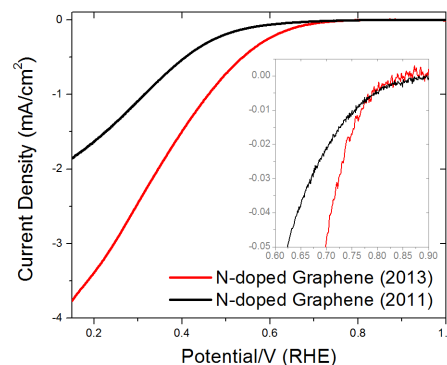


Figure 3. LSVs of N-doped graphene foams.

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