Electrochemical oxygen reduction on nitrogen-doped graphene powder

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Fuel cells have the potential to help wean our global society off its dependence on fossil fuels. However there are several major obstacles to the widespread acceptance of fuel cells in transport, homes and mobile devices. One of the major barriers is the cost of fuel cell systems. This is largely due to the high price and rarity of the platinum catalyst used for oxygen reduction and hydrogen oxidation.

An interesting alternative to platinum are Fe/N/C-based materials which have been shown to be strongly active for electrochemical oxygen reduction,[1] with impressive durability and performance in fuel cells.[2] Such materials are often fabricated by pyrolysis, milling and acid washing of blends of polymers and iron sources. However, the nature of the active site in this class of materials is still much debated; especially as to whether Fe atoms are involved in 4-electron oxygen reduction, or if carbon-nitrogen conjugation alone can catalyze 4-electron oxygen reduction. Simulations suggest that carbon and nitrogen alone can be active; in particular when a nitrogen atom is at a quaternary position adjacent to a zigzag carbon edge.[3] This has been backed up by several experiments in which efficient electrochemical oxygen reduction has been observed in iron-free nitrogen-doped carbon materials.[4]

Here we explore a relatively new material for electrochemical oxygen reduction; nitrogen-doped graphene. Graphene has recently taken the scientific world by storm and a long list of beneficial applications is stacking up. One of the reasons for the success of graphene is its impressive material and electronic properties. For example, it has high surface area, conductivity, hydrophobicity, and stability. These assets in particular make it an ideal for electrochemical applications.

Nitrogen-doped graphene was prepared by a solvothermal chemical reaction between sodium and ethanolamine in a Teflon chamber, followed by flash pyrolysis in air at 600˚C and washing. After this the material was characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), BET nitrogen adsorption analysis, and linear sweep voltammetry (LSV).

TEM images (Fig. 1) show that the product is a foam-like powder, with graphene making up the domain walls, corresponding well with the literature. AFM (not shown) revealed that the thickness of the individual graphene domain-walls was 1.7 nm, corresponding to ~ 2 atomic layers. XPS of the material showed that the nitrogen content decreased with increasing pyrolysis temperature, as expected, from 9.4 at.% at 600˚C to 2.5 at.% at 1000˚C. The large peak at ~ 400.5 eV suggests that a large proportion of quaternary nitrogen is present in the material. The surface areas for samples pyrolysed at 600, 800 and 1000˚C were 60, 161 and 170 m^2/g, respectively.

Linear sweep voltammetry can give information about the oxygen reduction activity of a catalyst. Here, the data were measured in acid media. It can be seen that after pyrolysis over 800˚C the oxygen reduction current density is high. This high activity is attributed to the increase in surface area and conductivity associated with pyrolysis. By measuring the amount of H_2O_2 produced during the measurement, the average number of electrons per oxygen reduction event was determined to the ~3, indicating a mixture of 2 and 4 electron oxygen reduction.

These results have potential for improvement, show that some degree of 4 electron oxygen reduction can be observed even in Fe-free materials, and highlight graphene as an interesting material for electrochemistry.

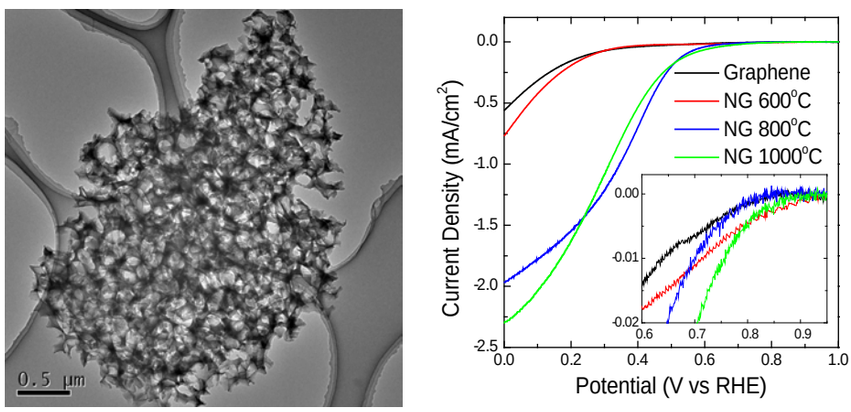

Figure 1. TEM of nitrogen-doped graphene foam.

Figure 3. LSVs of nitrogen-doped graphene powder pyrolysed at 600, 800 and 1000˚C, and undoped graphene.

[1] Nabae, Y. et al. *Carbon* **2010,** *48*, 2613-2624.
[2] Libin W. et al. *Chem. Commun*., **2010**, 46, 6377-6379.
[3] Niwa, H. et al. *Journal of Power Sources* **2009,** *187*, 93–97.
[4] Lyth, S. M. et al. *J. Electrochemical Soc.* **2011,** *158*, B194-B201.