Understanding Functionalised Carbon Electrocatalysts for Oxygen Reduction Reaction

K. Polus[1], A. Walton[2]

[1,2] *The University of Manchester, UK*

kacper.polus@manchester.ac.uk

Oxygen reduction reaction (ORR) is an electrochemical half-reaction with an industrial importance in hydrogen fuel cells where it is responsible for conversion of oxygen from air into aqueous species. ORR is intrinsically sluggish, therefore, it requires an efficient catalyst. Current state-of-the-art ORR catalyst is platinum-based, which makes it undesirable due to low availability of the precious metal and unsustainable extraction practices. Carbon-based catalysts, doped with heteroatoms, have been demonstrated to show significant electrocatalytic activity towards ORR, which could compete with platinum. However, further efforts are required in order to understand the electrocatalytic mechanisms of ORR using carbon catalysts and to devise a catalyst exhibiting electrocatalytic activity matching that of platinum.

In a study focused on a state-of the-art ORR catalyst, iron- and nitrogen- co-doped pyrolytic carbon (Fe-N/C) has been studied using Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS). The catalyst was exposed to nitric oxide (NO) gas during spectra acquisition. NO interacts with the ORR active sites, therefore, it was possible to gain insight into the nature of the active sites in the Fe-N/C catalyst by observing N 1s signal during a NO exposure and varying temperature cross-study. A Near Edge X-ray Absorption Fine Structure (NEXAFS) experiment was done in order to gain complementary information about the nature of the active sites by observing Fe L-edge.

In a parallel model-system approach, a real ORR catalyst was approximated by placing a layer of iron-containing porphyrin molecules on top of a highly-oriented pyrolytic graphite surface. This strategy allows a more fundamental insight into the ORR mechanism due to a much lower level of complexity of the system, yielding information coherent with the real-catalyst study.

Overall, presented here is a significant experimental insight to a system which to date has only been studied by computational simulations.