**Chemical Nature of Catalytic Active Sites for the Oxygen Reduction Reaction on Nitrogen-Doped Carbon-Supported Non-Noble-Metal Catalysts[[1]](#footnote-1)**

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The oxygen reduction reaction (ORR) is an essential reaction in electrochemistry because of its importance in cathodic reaction in polymer electrolyte membrane fuel cells (PEMFCs), a clean and sustainable high energy density power source. Pt and Pt-based alloy catalysts have long been regarded as the best catalysts for the four-electron oxygen reduction reaction (O2 + 4H+ + 4e– → 2H2O). However, the kinetics of the ORR on Pt-based catalysts are sluggish; the Pt catalysts have poor durability, and the costs of Pt catalysts are too high. To address these issues with Pt, one promising strategy is to design and synthesize a non-noble-metal catalyst such as a nitrogen-doped carbon-supported transition metal (metal–N–C catalysts) catalyst.

The open literature describing non-noble metal catalysts dates back to 1964, when Jasinski[1] reported the use of metal phthalocyanine-complexes as substitutes for expensive Pt-based catalysts. Following Jasinski’s discovery, it was demonstrated that a significant increase of catalyst stability and activity (improved by several orders of magnitude) could be achieved by thermal treatment of these phthalocyanine- and porphyrin-based materials.[2,3] Next, Gupta et al.[4] demonstrated that ORR activities achieved by thermal treatment of metal macrocycles could also be obtained with nitrogen-doped carbon-supported cobalt catalysts, which were synthesized by heat-treating a mixture of Co(II) salt and polyacrylonitrile. Gupta’s results showed that the precursor to pyrolysis need not be a metal in a macrocycle structure (like phthalocyanine and porphyrin) in order to get an active non-noble metal catalyst.

Following the above works, numerous nitrogen-doped carbon-supported metal catalysts (especially Fe and Co in metal-nitrogen-carbon networks) have been now synthesized and studied in attempts to find non-noble metal catalysts with improved catalytic activity for the ORR. These non-noble metal catalysts are often synthesized by pyrolysis of transition metal salts with nitrogen-containing molecules or polymeric organic precursors.

However, the exact nature of the active sites in the metal–N–C catalysts is still controversial and remains unsolved until today. The objective of this work is to study the nature of active sites for ORR in the Fe–N–C catalysts. We synthesized a new family of nitrogen-doped carbon with iron catalysts (denoted as Fe–N–C catalysts) by pyrolyzing the mixtures with various ratios of a nitrogen-atom rich heterocycle compound, 1-ethyl-3-methylimidazolium dicyanamide (EMIM-dca), and iron chloride (FeCl3). The ORR activity (*J*K at 0.8 V vs RHE, in 0.1 M KOH solution) of a typical catalyst, Fe15–N–C1000, in this family is 6.65 mA/mg, which is much higher than the values of the Fe–C (0.48 mA/mg) and N–C catalysts (0.25 mA/mg). The relationship between the ORR activity and the structures (the possible active sites in particular) of the catalysts was studied under different conditions. The active site in the catalyst is found to be the Fe–N species (most likely in the form of Fe3N). Metallic iron (Fe) particles, Fe3C species, and N–C species are not catalytically active sites, nor do these moieties interact with the Fe–N active sites during the catalysis of the ORR. High pyrolysis temperatures and increasing the Fe content during the synthesis favor the formation of the Fe–N active sites in the final catalyst. Our study opens up new synthetic control of parameters affecting the final structure and catalyst performance, and allows modifying the unexplored avenues toward new multiply heteroatom doped nonprecious ORR catalysts.

**References**

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