

A Solid State NMR Study of Polyaniline-Fe Non-Precious Metal Cathode Catalysts for Oxygen Reduction in Fuel Cells

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Polymer electrolyte fuel cells (PEFCs) are attracting increasing attention as environmentally benign power sources for both stationary and mobile applications. The oxygen reduction reaction (ORR) at the cathode is a sluggish and complicated four-electron process. Carbon-supported platinum (Pt/C) is widely used in cathode catalysts for ORR[1, 2]. However, even on pure Pt, the overpotential for ORR is in excess of 300 mV. In addition, Pt is a precious metal of the lowest abundance and it is thus of great interest to develop Pt-free cathode catalysts for PEFCs.

Several Pt-free materials have been proposed as potential alternative catalysts for ORR, such as Ru/Ir-based chalcogenides[3], Pd-based alloys[4], transition metal oxides[5], and carbides and nitrides[6]. Jasinski[7] first reported that transition metal porphyrins and phthalocyanines display electrocatalytic activity towards ORR. More recently, it has been found that active ORR catalysts can be synthesized by pyrolyzing a wide variety of transition metal, carbon and nitrogen-containing precursors at high temperature [8-12].

In our previous work, iron-containing and iron-free ¹⁵N labeled polyaniline (PANI) is prepared as a precursor of N-doped carbon catalysts and is pyrolyzed at several different temperatures in a nitrogen atmosphere. The iron-free pyrolyzed PANIs display quite poor catalytic activity for ORR, whilst the iron-containing pyrolyzed PANIs display better ORR activity [12].

In the present study, the evidence of the existence of iron ion (Fe²⁺ or Fe³⁺) is found in our iron-containing PANI catalysts, and further the nitrogen of ligands is also observed in ¹⁵N solid state NMR.

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