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PAPER

Structure of the catalytic sites in Fe/N/C-catalysts for O_2-reduction in PEM fuel cells†

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Fe-based catalytic sites for the reduction of oxygen in acidic medium have been identified by ^{57}Fe Mössbauer spectroscopy of Fe/N/C catalysts containing 0.03 to 1.55 wt% Fe, which were prepared by impregnation of iron acetate on carbon black followed by heat-treatment in NH_3 at 950 °C. Four different Fe-species were detected at all iron concentrations: three doublets assigned to molecular FeN_4-like sites with their ferrous ions in a low (D1), intermediate (D2) or high (D3) spin state, and two other doublets assigned to a single Fe-species (D4 and D5) consisting of surface oxidized nitride nanoparticles (Fe_xN, with $x \leq 2.1$). A fifth Fe-species appears only in those catalysts with Fe-contents ≥ 0.27 wt%. It is characterized by a very broad singlet, which has been assigned to incomplete FeN_4-like sites that quickly dissolve in contact with an acid. Among the five Fe-species identified in these catalysts, only D1 and D3 display catalytic activity for the oxygen reduction reaction (ORR) in the acid medium, with D3 featuring a composite structure with a protonated neighbour basic nitrogen and being by far the most active species, with an estimated turn over frequency for the ORR of 11.4 e^- per site per s at 0.8 V *vs.* RHE. Moreover, all D1 sites and between 1/2 and 2/3 of the D3 sites are acid-resistant. A scheme for the mechanism of site formation upon heat-treatment is also proposed. This identification of the ORR-active sites in these catalysts is of crucial importance to design strategies to improve the catalytic activity and stability of these materials.

Broader context

H_2/O_2 (air) polymer electrolyte membrane fuel cells (PEMFCs) are clean and efficient electrical power generators that have been repeatedly demonstrated as a viable alternative to combustion engines for automobile propulsion. However, the cost of automotive fuel cells remains prohibitively high because of the quantity of platinum needed for fuel cell electrodes. Since the majority of platinum resides at the cathode (the electrode where oxygen is reduced to water) the substitution of the Pt-catalyst with an inexpensive material would significantly reduce the manufacturing cost of this electrode. Recently, our group reported molecular-based Fe/N/C cathode catalysts with high activity for the oxygen reduction reaction (ORR) and enhanced mass transport properties to generate useful currents at meaningful fuel cell voltages for automotive applications. The long standing durability shortcomings of such Pt-free-based catalysts for ORR have also been addressed to some degree. However, despite five decades of intensive research to replace Pt at the cathode of PEMFCs, no consensus has yet been reached regarding the exact identity of the catalytic species at work in these catalysts. We believe that the lack of consensus in this matter stems from the large variety of species, metal-containing or not, that are produced during the pyrolysis step necessary to obtain these catalysts. In this work, it will be shown that only a few of these species exhibit catalytic activity for the ORR in Fe/N/C. Identifying these species and acquiring knowledge about their molecular structure is now essential for improving their activity and durability.

Introduction

In recent years, the growing scarcity of easily accessible oil and its disproportionate geographical distribution have spurred

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