

Unveiling N-Protonation and Anion-Binding Effects on Fe/N/C Catalysts for O₂ Reduction in Proton-Exchange-Membrane Fuel Cells

Juan Herranz,[†] Frédéric Jaouen,^{*,†} Michel Lefèvre,[†] Ulrike I. Kramm,^{†,‡} Eric Proietti,[†] Jean-Pol Dodelet,[†] Peter Bogdanoff,[‡] Sebastian Fiechter,[‡] Irmgard Abs-Wurmbach,[§] Patrick Bertrand,^{||} Thomas M. Arruda,[⊥] and Sanjeev Mukerjee[⊥]

[†]Institut National de la Recherche Scientifique, Énergie, Matériaux et Télécommunications, Varennes, Québec, J3X 1S2, Canada

[‡]Helmholtz-Zentrum Berlin für Materialien und Energie Lise-Meitner-Campus, Institute for Solar Fuels and Energy Storage (E-I-6), Hahn-Meitner-Platz 1, D-14109, Berlin, Germany

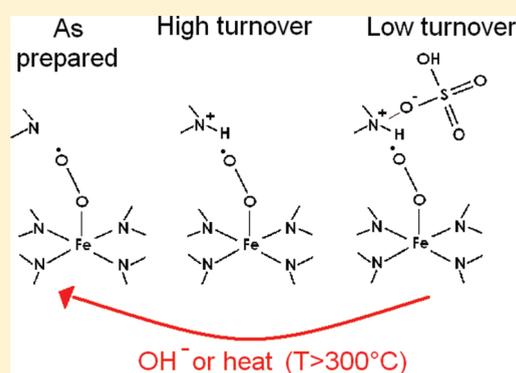
[§]Technical University Berlin, Faculty VI, Ackerstrasse 76, D-13355, Berlin, Germany

^{||}Université Catholique de Louvain, Institut de la Matière Condensée et des Nanosciences, Croix-du-sud 1, 1348 Louvain-la-neuve, Belgium

[⊥]Department of Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts 02115, United States

S Supporting Information

ABSTRACT: The high cost of proton-exchange-membrane fuel cells would be considerably reduced if platinum-based catalysts were replaced by iron-based substitutes, which have recently demonstrated comparable activity for oxygen reduction but whose cause of activity decay in acidic medium has been elusive. Here, we reveal that the activity of Fe/N/C catalysts prepared through a pyrolysis in NH₃ is mostly imparted by acid-resistant FeN₄ sites whose turnover frequency for the O₂ reduction can be regulated by fine chemical changes of the catalyst surface. We show that surface N-groups protonate at pH 1 and subsequently bind anions. This results in decreased activity for the O₂ reduction. The anions can be removed chemically or thermally, which restores the activity of acid-resistant FeN₄ sites. These results are interpreted as an increased turnover frequency of FeN₄ sites when specific surface N-groups protonate. These unprecedented findings provide a new perspective for stabilizing the most active Fe/N/C catalysts known to date.



1. INTRODUCTION

Proton-Exchange-Membrane Fuel Cells (PEMFCs) are well-suited electrical power generators for portable and automotive applications due to their high efficiency, high power density, and low operating temperature. While this technology is being deployed in niche markets, its cost remains prohibitive for widespread commercialization, especially for automotive propulsion. On the basis of a production volume of 500 000 automotive PEMFC units, it is predicted that the Pt-based catalyst would account for half of the PEMFC stack cost.¹ Due to the slow kinetics of the Oxygen Reduction Reaction (ORR), 90% of the platinum in the latest H₂/air PEMFCs is needed at the cathode.² Hence, the development of nonprecious metal catalysts with high ORR activity and durability has become a major focus in recent years.

After it was first discovered that cobalt-phthalocyanine was active toward the ORR,³ progress continued with the finding that a heat treatment above 600 °C increased the activity of catalysts based on metal-N₄ macrocycles.⁴ It was later reported that similar activity could be achieved by heat treating catalyst precursors

made simply of (i) a transition metal salt, (ii) nitrogen, and (iii) carbon.^{5–7} Among the transition metals in period 4, iron produces the most active catalysts in acidic medium, referred to as Fe/N/C catalysts because of the spectroscopic evidence of FeN₄ moieties.^{8–12} In 2009, our group reported on an innovative synthesis that remarkably increased the activity of Fe/N/C catalysts but not their durability.¹³ Stable currents in PEMFCs for less active Fe/N/C-based cathodes have, however, been demonstrated for 60–200 h at 0.5 V^{6,14} and recently for 280–600 h at 0.4 V.^{15,16} Therefore, bridging the gap between the attributes responsible for high activity and high durability has become the main challenge facing Fe/N/C catalysts.¹⁷

The present work reveals that (i) some FeN₄ sites located on the catalyst's top surface are structurally stable in acidic medium, (ii) specific N-groups on the catalyst surface (and not involved in Fe coordination) protonate in acidic medium and bind anions,

Received: May 7, 2011

Revised: July 11, 2011

Published: July 12, 2011