

In situ Spectroscopic Observation of the Fe-N₄ and Fe-N₂₊₂ Sites during Oxygen Reduction

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Despite the significant progress made in the development of M-N_x/C catalysts, the exact nature of the active sites formed during pyrolysis, as well as the reaction mechanisms remains unclear. In this work, x-ray absorption spectroscopy (XAS) measurements were performed on the two state-of-the-art PANI-derived catalysts,¹ PVAG-Fe-NEU,² and FeTPP/C pyrolyzed at various temperatures.³ EXAFS fits in combination with $\Delta\mu$ -XANES analysis are used to reveal the atomic structure of the catalysts and understand the precise structural effects on the ORR activity and reaction mechanism. The $\Delta\mu$ technique has evolved into a powerful tool for elucidating surface adsorbed species in electrocatalysis and involves comparison of theoretically simulated signatures of subtracted XANES spectra (surface with and without adsorbed species) and those experimentally derived using spectral subtraction of data measured at different potentials.^{4,5}

As shown in Fig. 1a, the first shell coordination numbers (CNs) of all the catalysts are increased by ~1 when the operating potential increases from 0.3 to 0.9 V, indicating most of the Fe-N₄ sites are covered by OH at 0.9 V. The lower CNs for PANI-derived catalysts are due to the co-existence of the nano-scaled metallic Fe or Fe oxides that do not have surrounding nitrogen atoms.

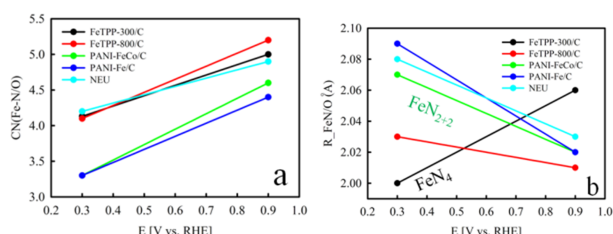


Fig. 1 The coordination number (a) and the Fe-N/O bond distance (b) for the catalysts indicated obtained in 0.1 M HClO₄ at 0.3 V and 0.9 V.

As shown in Fig. 1b, the Fe-N/O bond distance of FeTPP-300/C (pyrolyzed at 300 °C) increase from ~2.00 to ~2.06 Å when the operating potential is increased from 0.3 to 0.9 V, which indicates the in-plane iron atom shifts away from the plane towards the axially bound OH as widely observed for non-pyrolyzed NPM catalysts. On the contrary, the Fe-N/O bond distances of PANI-derived and PVAG-Fe-NEU catalysts decrease from >2.07 to ~2.02 Å, which indicates the Fe²⁺ ion locates out of the N₄-plane, and shifts back into the plane due to the axially bound OH. The $\Delta\mu$ analysis show while the FeTPP-300/C is dominated by Fe-N₄ site that the central iron atom is coordinated by four pyrrolic nitrogen atoms, the PANI-derived and PVAG-Fe-NEU catalysts are mainly composed of Fe-N₂₊₂ site in which the central iron atom is coordinated by four pyridinic nitrogen atoms. The Fe-N₂₊₂ switching behavior favors oxygen molecule dissociation and oxygenated adsorbate (OH) desorption, and thus is the origin of the enhanced ORR activity relative to Fe-N₄.

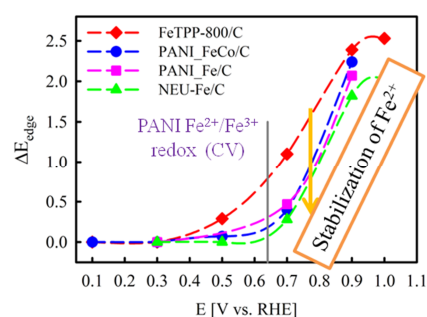


Fig. 1 Plots of ΔE_{edge} vs potential for indicated catalysts. The grey vertical line locating at the redox potential of PANI-derived catalysts (0.64 V) is drawn as a guide to the eye.

The XANES at the Fe K edge provides a direct measure of the oxidation state of the iron center. As shown in Fig. 2, the transitions from Fe²⁺ to Fe³⁺ oxidation state, manifested by the absorption edge shifts towards higher energies with increasing potentials coincide with the redox potentials obtained electrochemically. This Fe^{2+/3+} transitions are accompanied with the adsorption of OH as determined by EXAFS. Therefore, the enhanced ORR activity of pyrolyzed samples as estimated by the higher onset potential (or low overpotential) is attributed to the suppression of O(H) adsorption from water activation or the stabilization of Fe²⁺ oxidation state at high potential, similar to the well understood ORR enhancement mechanism of Pt-based alloys. The similarity of the ORR kinetics between the iron-based and Pt-based catalysts is further supported by the fact that the OH coverage trend as a function of potential matches the theoretical O(H) trend predicted on Pt-based systems.⁶

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- (1) Wu, G.; More, K. L.; Johnston, C. M.; Zelenay, P. *Science* **2011**, 332, 443-447.
- (2) Tylus, U.; Ramaswamy, N.; Jia, Q.; Mukerjee, S. *Meeting Abstracts* **2012**, 225-225.
- (3) Ramaswamy, N.; Mukerjee, S. *Advances in Physical Chemistry* **2012**, 2012, 17.
- (4) Roth, C.; Benker, N.; Buhrmester, T.; Mazurek, M.; Loster, M.; Fuess, H.; Koningsberger, D. C.; Ramaker, D. E. *J. Am. Chem. Soc.* **2005**, 127, 14607-14615.
- (5) Jia, Q.; Ramaker, D. E.; Ziegelbauer, J. M.; Ramaswamy, N.; Halder, A.; Mukerjee, S. *The Journal of Physical Chemistry C* **2013**, 117, 4585-4596.
- (6) Rossmeisl, J.; Karlberg, G. S.; Jaramillo, T.; Norskov, J. K. *Faraday Discuss.* **2009**, 140, 337-346.