

Catalytic Roles of Fe-N_x and Fe-Fe₃C@C Species in Fe-N/C Electrocatalysts for Oxygen Reduction Reaction

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The development of active and durable non-precious metal-based oxygen reduction reaction (ORR) catalysts has been of prime importance for renewable-energy technologies including fuel cells and metal-air batteries. Iron and nitrogen co-doped carbons (Fe-N/C) have been considered as the most promising candidates among non-precious metal ORR catalysts, owing to their outstanding ORR activity, but the catalytic role of active species in Fe-N/C catalysts is still a subject of debates. Although there has been a consensus that Fe-N_x sites play a significant role in the ORR, recently iron and/or iron carbide encased within carbon shells (Fe-Fe₃C@C) has also been suggested as an active species for the ORR. However, a broad spectrum of possible roles has been proposed for the Fe-Fe₃C@C species. Some groups reported that high ORR activity could be achieved with catalysts containing only Fe-Fe₃C@C sites [1]. Others suggested that the Fe-Fe₃C@C sites play a synergistic role in conjunction with the Fe-N_x sites [2]. Another viewpoint is that Fe-Fe₃C@C sites are merely an impurity phase [3]. Such a discrepancy is stem from similarity of synthetic route between Fe-N_x and Fe-Fe₃C@C sites, hampering the identification of exclusive role of each species.

In this presentation, in order to establish the respective roles of Fe-N_x and Fe-Fe₃C@C sites we rationally designed model catalysts via the phase conversion reactions of Fe₃O₄ nanoparticles supported on carbon nanotubes. The resulting three catalysts selectively contained Fe-N_x, Fe-Fe₃C@C, and N-doped carbon (C-N_x) sites. The catalysts containing

Fe-N_x sites exhibited superior ORR activity with low HO₂⁻ yield (Fig. 1a), compared to other two catalysts. When Fe-N_x sites were etched by an acid or poisoned by CN⁻, the catalytic activity decreased drastically (Fig. 1a), confirming that Fe-N_x sites play a major role for high ORR activity via 4-electron (4 e⁻) pathway (Fig. 1b). On the other hand, the catalysts only with Fe-Fe₃C@C sites showed inferior ORR performance and high HO₂⁻ yield (Fig. 1a). Through additional peroxide reduction experiment, encapsulated form of Fe-Fe₃C@C sites could facilitate sequential peroxide reduction, concluding that Fe-Fe₃C@C sites play an auxiliary role for the ORR via 2 e⁻ × 2 e⁻ pathway (Fig. 1b).

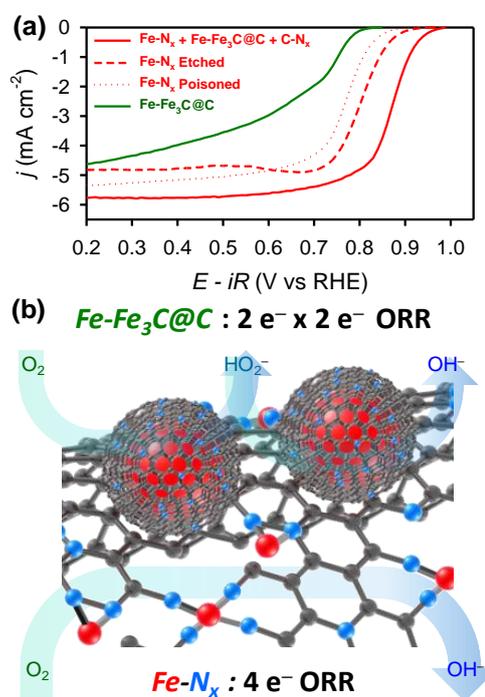


Fig.1 (a) ORR polarization curves of model catalysts. (b) Illustration of the role of Fe-N_x and Fe-Fe₃C@C sites for the ORR.

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