Rational Design of High-Performance M-N/C Electrocatalysts for Oxygen Reduction Reaction

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The development of highly active, durable, and low-cost oxygen reduction reaction (ORR) catalysts is central to making polymer electrolyte fuel cells commercially viable. During the last decade, tremendous recent efforts have been devoted to replacing expensive, scarce Pt-based electrocatalysts with non-precious metal catalysts (NPMCs) for the ORR. Among various NPMCs, M-N/C (M=Fe or Co) catalysts have emerged as the most promising ORR catalysts due to their high ORR activities. In this direction, we have endeavored toward the rational design of high-performance M-N/C catalysts and the identification of active species in M-N/C catalysts [1-6].

We have prepared a family of transition metal-doped ordered mesoporous porphyrinic carbons (M-OMPCs; M=Fe, Co, Ni, or their combinations) by nanocasting mesoporous silica templates with macrocyclic compounds such as metalloporphyrin and metallophthalocyanines [1-2]. The M-OMPC catalysts contain predominantly molecularly dispersed M-N$_x$ sites and have large surface areas and tunable pore structures. Among the M-OMPC catalysts, the FeCo-OMPC catalyst exhibited an excellent ORR activity in an acidic medium, higher than other non-precious metal catalysts.

We have developed a general design strategy based on "silica-protective-layer-assisted" method (Fig. 1) that can preferentially produce catalytically active Fe-N$_x$ sites towards highly efficient Fe-N/C electrocatalysts [3,4]. This method is applicable to any type of carbon supports as well as Fe-N precursors. One of resulting catalysts, consisting of CNT wrapped with thin porphyrinic carbon layer (CNT/PC), contained relatively high density of Fe-N$_x$ sites, and showed very high ORR activity and remarkable stability in alkaline media. Importantly, the CNT/PC-based cathode demonstrated excellent performances in both alkaline anion exchange membrane fuel cell as well as acidic proton exchange membrane fuel cell.
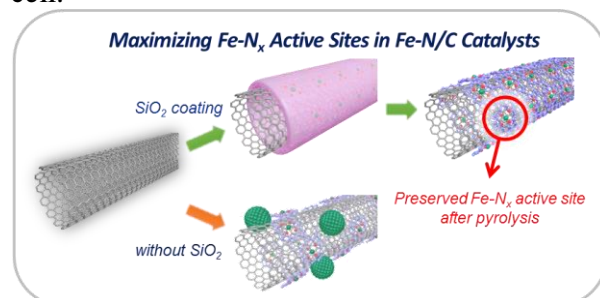

Fig.1. "Silica-protective coating" strategy toward high-performance M-N/C catalysts.

We have also made efforts toward identifying the active species in M-N/C catalysts [5]. We constructed archetypical hybrid catalysts by the reaction of an organometallic complex, [CoII(acac)$_2$] (acac=acetylacetonate), with N-doped graphene-based materials at room temperature. In the hybrid structure, the cobalt-containing species is coordinated to heterocyclic groups in N-doped graphene as well as to its parental acac ligands. The hybrid material shows high electrocatalytic activity for the ORR in alkaline media, and superior durability and methanol tolerance to a Pt/C catalyst. Based on the chemical structures and ORR experiments, we could identify a new active species for the ORR: "Co-O$_4$-N" structure.

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