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Active site of nitrogen-doped carbon catalysts for fuel cells

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Nitrogen-doped carbon materials exhibit high electrocatalytic activity for the oxygen reduction reaction (ORR) in polymer electrolyte fuel cells, which is essential for several renewable energy systems. However, the ORR active site(s) is unclear, which retards further developments of high-performance catalysts. There are controversies on the active sites of nitrogen-doped carbon catalysts. Major nitrogen species are pyridinic nitrogen and graphitic nitrogen, which are bonded with two and three carbon atoms, respectively. However, it is not clear which nitrogen species creates the active site for ORR. We have conclusively characterized the ORR active site by using newly designed graphite (HOPG) model catalysts with well-defined π -conjugation and well-controlled doping of nitrogen species [1]. The ORR active site is created by pyridinic N, while graphitic N-doped HOPG surfaces show no catalytic activity for ORR. CO₂ adsorption experiments indicated that pyridinic N also creates Lewis basic sites. The specific activities per pyridinic N in the HOPG model catalysts are comparable with those of N-doped graphene powder catalysts. It is thus concluded that the ORR active sites in nitrogen-doped carbon materials are carbon atoms with Lewis basicity next to pyridinic N. We have further examined the local electronic structure of the pyridinic N-doped HOPG surface by scanning tunneling spectroscopy (STS). As a result, a non-bonding pz state or edge state was observed by STS in the vicinity of the nitrogen atom, which is ascribed to the origin of the ORR activity.

[1] Donghui Guo, Riku Shibuya, Chisato Akiba, Shunsuke Saji, Takahiro Kondo, Junji Nakamura, *Science* 351, 366 (2016)