OXYGEN REDUCTION REACTION

Iron's bad company

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The deployment of fuel cells — electrochemical cells that convert chemical energy from a fuel into electricity — is becoming a reality and some vehicles are already commercially available. Of particular interest to the automotive industry are polymer electrolyte membrane fuel cells, due to their low operating temperature and rather high efficiency. These use hydrogen as a fuel and involve the oxygen reduction and hydrogen oxidation reactions at the cathode and the anode, respectively, the former being the limiting half-reaction because of its slow kinetics and high overpotential. The cathode catalyst relies on platinum-based materials and, therefore, significant research efforts have been devoted to decrease the content of this precious metal. Atomically dispersed iron on nitrogen-doped carbon (Fe–N–C) has emerged as a good alternative to platinum-based catalysts. However, the Fe–N–C catalysts suffer from deactivation via a mechanism that remains largely unknown.

Now, Frederic Jaouen, Hyungjun Kim, Chang Hyuck Choi and co-workers combine electrochemical, spectroscopic and

computational techniques to demonstrate that the deactivation of the Fe–N–C catalysts is linked to the reversible surface oxidation of carbon near the Fe–N_x sites. H₂O₂, the main by-product of the oxygen reduction reaction, induces a decrease in activity and four-electron selectivity due to the generation of reactive oxygen species via Fenton-like reactions in the acidic electrolyte. These species alter the carbon atoms in iron's second coordination shell by functionalization with oxygen, but leave intact the Fe–N_x active sites, which results in a decrease of the intrinsic activity — the turnover frequency — of the active sites due to a change in the electronic structure of the material. The comprehensive study reported by Jaouen, Kim, Choi and colleagues will surely encourage further work to avoid or minimize the impact of Fenton-like reactions and address the durability issues of Fe–N–C catalysts.

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