OXYGEN REDUCTION REACTION

(On-)site correlations

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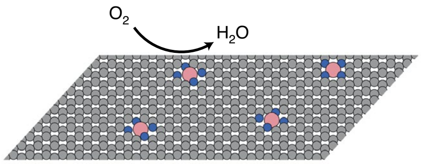

The deployment of proton-exchange membrane fuel cells (PEMFCs) is already becoming a reality. PEMFC devices, however, mostly rely on costly Pt to catalyse both the anodic and cathodic reactions, which represents a significant portion of the total fuel cell stack cost. Decreasing the amount of — or even removing completely — Pt would have a substantial economic impact, and therefore the design of Pt-free — or more generally, Pt group metal (PGM)-free — catalysts has recently attracted a great deal of attention. The more sluggish reaction, the reduction of molecular oxygen, takes place at the cathode, for which atomically-dispersed metal atoms on a nitrogen-doped carbon matrix (M–N–C, where M can be Fe, Co or Mn, but most prominently Fe) are a very promising catalyst class to replace PGM-based materials.

Now, a cross-national collaboration with teams across Europe and the United States, also involving the industrial partner Johnson Matthey, have presented a thorough evaluation of four Fe–N–C catalysts prepared by different laboratories — CNRS/University of Montpellier (CNRS), Imperial College London (ICL), University of New Mexico (UNM) and Pajarito Powder Inc. (PAJ) — in a round robin test manner. The four catalysts have been synthesized via different protocols and present distinctive fingerprints upon characterization by N_2 sorption, X-ray photoelectron spectroscopy and ^{57}Fe Mössbauer spectroscopy. The study made use of two recently developed approaches to estimate the Fe active site density (SD) — namely, ex situ CO cryo chemisorption and in situ electrochemical NO_2^- stripping. The catalytic performance was evaluated using a rotating ring-disc electrode in O_2-saturated 0.5 M H_2SO_4 electrolyte, from which turnover frequencies (TOFs) were derived.

While the CNRS catalyst generally shows the highest SD, it exhibits the lowest TOF — on the flip side, the PAJ catalyst displays the opposite trend. The researchers then put forward a set of interesting correlations of SD and TOF with features such as micropore volume, Fe content, pyridinic/pyrrolic nitrogen content or specific FeN_x site content — D1, D2 or D1 + D2, as derived from the Mössbauer assignment. Finally, the ratio of Fe sites located at the catalyst pore surface was estimated and coined as the site utilization factor. The PAJ catalyst exhibited the highest site utilization factor of 80%, which decreased to 10% under working conditions, while the ICL catalyst displayed the lowest value of 20% ex situ, decreasing to 8% under in situ conditions.

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