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# STABILIZATION OF Fe-N<sub>4</sub> SITES BY PLATINUM DURING OXYGEN REDUCTION IN ACID MEDIUM

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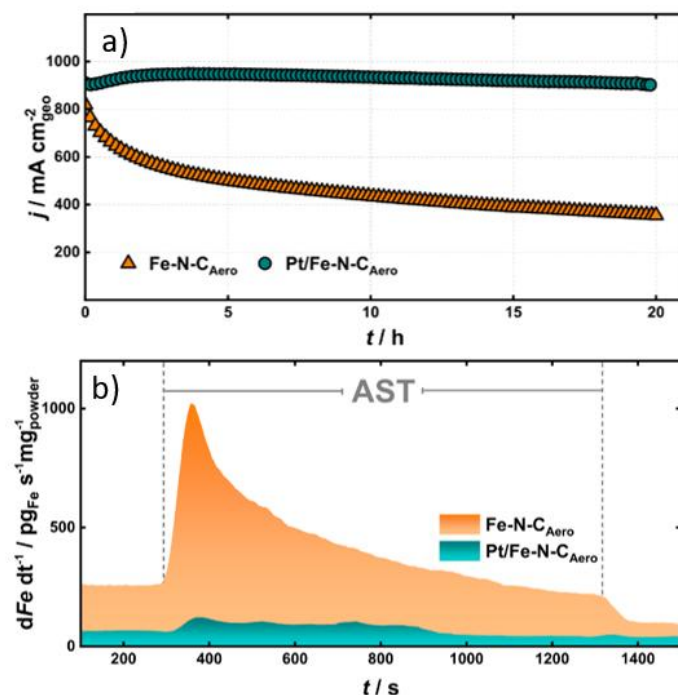
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The deployment of proton-exchange-membrane fuel cells is hindered by the large amount of Pt required for anode and cathode electrocatalysis. While Fe–N–C materials have shown promising initial oxygen reduction reaction (ORR) activity, they lack durability. Key degradation mechanisms include direct demetallation of FeN<sub>4</sub> sites and indirect deactivation caused by reactive oxygen species. Enhanced durability of Fe–N–C materials can be achieved by interfacing them with a low amount of Pt nanoparticles (NPs) or even Pt single atoms.<sup>1-2</sup> The original idea was to lean on the known activity of bulk Pt and Pt NPs towards H<sub>2</sub>O<sub>2</sub> electroreduction. However, different Pt and Fe active sites can emerge in the current process for preparing Pt/Fe-N-C hybrid materials due to a relatively high-temperature step needed to reduce the Pt salt, leading to the transformation of some Fe-N<sub>4</sub> sites into Pt@FeO<sub>x</sub> core-shell structures, etc.

The presentation will show that it is possible to add controlled amounts of Pt NPs (0.25-2.0 wt. %) via a soft polyol method, resulting in unmodified Fe coordination, well-defined Pt structures and stable Pt/Fe–N–C hybrids. The approach is first validated for various mainstream Fe–N–Cs, including ZIF-8-derived Fe-N-C, aerogel derived Fe-N-C and silica-templated Fe-N-C.

With *operando* techniques, we demonstrate that the Pt addition nearly suppresses H<sub>2</sub>O<sub>2</sub> production during ORR and strongly reduces the Fe leaching rate during ORR, while *post mortem* Mössbauer spectroscopy reveals that the highly active but unstable Fe(III)N<sub>4</sub> site is partially stabilized.

The similar H<sub>2</sub>O<sub>2</sub> electroreduction activity of Pt/Fe–N–C and Fe–N–C and other analyses point toward a long-distance electronic effect of Pt NPs in stabilizing FeN<sub>4</sub> sites. This key stability property of Fe-N<sub>4</sub> sites during ORR brought by a low amount of Pt is experimentally elusive to understand. Possible synergistic effects between Pt and FeN<sub>4</sub> sites were further studied with density functional theory and a proposed mechanism will be presented that could explain the experimental observations.



**Fig. 1.** Characterization of catalysts in PEMFC or in gas diffusion electrode (GDE) setup. a) Chronoamperometry at  $U = 0.5$  V, b) Online ICP-MS results conducted in a GDE setup in  $O_2$ -saturated 0.1 M  $HClO_4$  electrolyte, the Fe dissolution rates of  $Fe-N-C_{Aero}$  and  $Pt/Fe-N-C_{Aero}$  were normalized to catalyst loading during an accelerated stress test consisting of 200 square cycles of 3.2 s at  $-49.7$   $mA \cdot cm^{-2}$  and 2.1 s at  $-0.1$   $mA \cdot cm^{-2}$ . The aerogel-derived Fe-N-C catalyst ( $Fe-N-C_{Aero}$ ) has an Fe content of 1.25 wt. %, and 1 wt.% Pt nanoparticles was deposited onto it to form the  $Pt/Fe-N-C_{Aero}$  hybrid.

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