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Electrochemical probing into the active sites of graphitic-layer encapsulated iron oxygen reduction reaction electrocatalysts

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Abstract

The graphitic-layer encapsulated iron-containing nanoparticles (G@Fe) have been proposed as a potential type of active and stable electrocatalysts for the oxygen reduction reaction (ORR). However, the contribution of the encapsulated components to the ORR activity is still unclear compared with the well-recognized surface coordinated FeN_x/C structure. Using the strong chelating effect of the iron component with anions, cyanide (CN^-) in alkaline and thiocyanate (SCN^-) in acidic media, the metal containing active sites are electrochemically probed. Three representative catalysts are chosen for a comparison including the as-prepared encapsulated G@Fe, commercial Fe/N/C catalyst with iron-nitrogen coordinated surface functionalities and molecular iron phthalocyanine (FePc) containing well-defined structures and compositions. It was found that the G@Fe catalyst showed the weakest poisoning effect (the lowest shifts of half-wave potential) compared to the Fe/N/C and FePc catalysts in both electrolytes. These results confirm the involvement in the ORR catalysis of encapsulated iron components in addition to the FeN_x/C surface functionality.

Keywords: encapsulated Fe catalysts, oxygen reduction reaction, ion poisoning, active sites