

Evolution of Active Sites in Iron Phthalocyanine Functionalized Carbon during Pyrolysis: Transforming into Active Fe-N_x-C Electrocatalysts for Oxygen Reduction Reaction

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Fe-N_x-C electrocatalysts for the oxygen reduction reaction (ORR) are primarily produced via atmosphere-controlled pyrolysis at high temperatures. Despite being the main methodology for the formation of an active site structure in the electrocatalyst, it remains a poorly understood phenomenon. At its core, in materials science, the processing conditions of a material determines its structure, which in turn influences its performance. Therefore, a systematic study was undertaken to analyze the influence of the pyrolysis conditions i.e. temperature and atmosphere on the nucleation, evolution and transformation of active sites in the development of Fe-N_x-C during the pyrolysis of an iron phthalocyanine (FePc)-functionalized carbon black. State-of-the-art *in situ* and *ex situ* characterizations confirmed that the atomic level dispersion of Fe-N_x type moieties remains up to 600 °C, from which iron oxide nanoparticles start forming and continue to grow over the course of the pyrolysis. Remarkably, different fingerprints acquired during in-situ and ex-situ X-ray absorption spectroscopy probed the attachment of oxygen as a fifth ligand on the Fe-based sites upon exposure to the open room environment. Using the rotating ring disc electrode (RRDE) technique, the ORR activity was elucidated in acidic and alkaline conditions, with the best activity observed when Fe-N_x-C was pyrolyzed at 600 °C. However, as the pyrolysis temperature is increased passed the threshold of 600 °C, the ORR activity decays drastically with a categorical alteration in the reduction route, shifting from a tetra-electronic to bi-electronic fashion. To evaluate this discrepancy, surface-to-reactivity analysis was performed ascertaining the relationship between the surface chemistry/morphology and electrocatalytic parameters.

References

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