

Evolution of Fe-N-C Oxygen Reduction Reaction Electrocatalyst during Pyrolysis: A Processing-Structure-Performance Relationship

*Mohsin Muhyuddin¹, Alessandro Lavacchi², Laura Capozzoli², Enrico Berretti², Eamonn Murphy³, Shengyuan Guo³, Plamen Atanassov³, Carlo Santoro¹

¹Department of Material Science, University of Milan Bicocca, U5, Via Cozzi 55, 20125 Milan, Italy

²Institute of Chemistry of Organometallic Compounds – National Research Council of Italy (ICCOM-CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino (Florence), Italy

³Chemical and Biomolecular Engineering, National Fuel Cell Research Center, University of California, Irvine, Irvine, California 92697, United States

*Mohsin Muhyuddin: e-mail: m.muhyuddin@campus.unimib.it

Abstract

Despite their lead over contemporary energy conversion technologies, fuel Cells are still far from commercial maturity due to the complexity and sluggishness of oxygen reduction reaction (ORR) taking place at the cathode. In this optics, Iron-Nitrogen-Carbons (Fe-N-Cs) are coming to light as a competent candidate to launch the ORR with appreciable kinetics without relying on expensive and scarce noble metals. Pyrolysis is often employed as the practice of choice for fabricating Fe-N-Cs where various sorts of iron, nitrogen and/or carbon precursors have been utilized to uplift the ORR performance. However, pyrolysis is itself a poorly understood and mysterious phenomenon. From the core of materials science; it is the fabrication route that defines the structural evolution and ultimately dictates the overall electroactivity of the electrocatalyst. Therefore, a systematic study was initiated to elucidate the influence of pyrolysis conditions i.e. temperature (200-1000 °C) and atmosphere (Ar or Ar/H₂), on the morphological parameters and surface chemistry of the evolved electrocatalysts and methodically correlated with the electrochemical performance in alkaline and acidic media. By combining several advanced characterization techniques it was observed that pyrolysis conditions remarkably affect the nature and proportion of active moieties that collaboratively determine the pathway and kinetics of the ORR in varying electrolytic media. X-ray diffraction (XRD) indicated that a slightly reducing atmosphere of Ar/H₂ inhibits the crystallographic growth of iron-based nanoparticles while a neutral atmosphere of pure Ar substantially affected the integrity of the atomically dispersed Fe in defective carbon as diffraction peaks corresponded to Fe₃O₄ tended to emerge after 600 °C. In-depth morphological examination through high-resolution-transmission electron microscopy (HR-TEM) further endorsed such discrepancies. Moreover, X-ray photoelectron spectroscopy (XPS) revealed multitudinous nitrogen-based moieties with different proportions in the Fe-N-C developed at different temperatures and under different environments. Interestingly, the samples pyrolyzed in a slightly reducing atmosphere showed an increasing trend of Fe-N_x with respect to pyrolysis temperature whereas in the samples fabricated under flowing Ar, Fe-N_x showed a positive relationship with temperature but their proportion started plummeting after 600 °C. On the other hand, graphitic nitrogen drastically increases after 700 °C in both scenarios. As a final point, electrochemical investigation using a rotating ring disc electrode (RRDE) categorically revealed the dependence of performance parameters on the structural features that evolved during pyrolysis. In acidic media (0.5 M H₂SO₄), Fe-N-Cs synthesized at 600 °C under both Ar and Ar/H₂ conditions demonstrated the best performance, with half-wave potentials ($E_{1/2}$) of ca. 0.7 and ca. 0.72 V (vs RHE) while maintaining the direct tetra-electronic reduction of oxygen. A similar performance was observed in the alkaline environment (0.1 M KOH) where the highest onset potentials and $E_{1/2}$ were obtained by the Fe-N-Cs pyrolyzed in the range of 600 and 700 °C in both atmospheres i.e. Ar ($E_{1/2} \approx 0.89$ V vs RHE) and Ar/H₂ ($E_{1/2} \approx 0.87$ V vs RHE), but a prompt reduction in the performance was seen afterward. Peroxide production showed a positive trend with pyrolysis temperature and drastically increased after 800 °C, which might be related to the growth of iron oxide nanoparticles and transformation in the surface chemistry. This work presents a novel insight into the pyrolysis-assisted evolution of Fe-N-C electrocatalysts for the ORR with optimum performance.