

Iron-Nitrogen-Carbon Catalysts by Different Synthesis Approaches for Efficient Oxygen Reduction Reaction in Fuel Cells Applications

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Oxygen Reduction Reaction (ORR) catalysts are at the forefront of Proton Exchange Membrane Fuel Cells (PEMFCs) research, focusing on Fe-N-C catalysts. These materials, composed of metal single atoms embedded within nitrogen-doped carbon matrices, have emerged as a promising alternative to traditional platinum-based catalysts in PEMFCs.

In this work, we propose a synthesis strategy based on the employment of mesoporous silica as a template for the morphology and porosity of the catalyst. Thanks to the mixing and consequent heat treatment of carbon, nitrogen, and iron precursors together with the silica template, it is possible to reproduce the complementary structure of the silica template, achieving a catalyst with controlled morphology and porosity. One of the major issues related to this synthesis approach consists of the complete removal of the silica template. In this work, we propose three different approaches: the first two approaches rely on the effects of acid and basic washing methods for silica removal. Hydrofluoric acid (HF) is a highly effective method, because of its ability to react with silicon dioxide (SiO₂) to form silicon tetrafluoride (SiF₄) gas and water. Nevertheless, HF is extremely toxic and can cause severe health issues. To overcome this safety issue, we propose another approach based on hydrochloric acid (HCl). HCl alone is less effective than HF in dissolving silica because the reaction is relatively slower and incomplete. However, HCl can become more effective if combined with sodium hydroxide (NaOH) which dissolves silica converting it into soluble silicate species. The third approach consists in an acid-washing-free synthesis, where Teflon (PTFE) is mixed with the precursors and used to remove the sacrificial template thanks to the in situ Teflon decomposition performed at high temperatures. Another issue related to the synthesis of FeNC catalysts relies on the formation of iron nanoparticles during the heat treatment at high temperature, that can act as an inert mass obstructing the active sites and negatively impacting the catalytic performance. In this context, acid leaching plays again an important role. In particular, the acid reacts with the metal particles leading to soluble metal salts or complexes, finally removed through washings with deionized water. Here, we present three FeNC catalysts achieved with different synthesis strategies, starting from the shared sacrificial silica template approach: FeNC^{HF}, FeNC^{NaOH+HCl}, and FeNC^{Teflon}. The coordination of iron sites with nitrogen is identified by the XPS technique, while SEM (fig. 1) and EDX techniques have been used to check the hard template strategy. Moreover, nitrogen physisorption isotherms have been recorded to evaluate the surface area and pore size and distribution through BET and BJH models. X-ray diffractometry (XRD) (fig. 2) is used as a tool to check the presence of crystalline phases in the Fe species. Finally, the ORR activity and selectivity have been evaluated through Rotating Ring Disk Electrode (RRDE) measurements in both alkaline (fig. 3) and acidic environments.

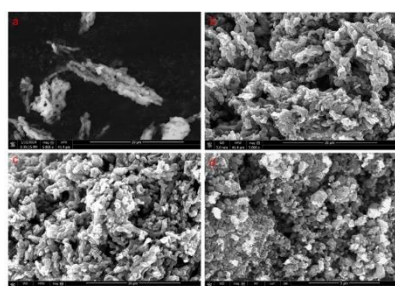


Fig. 1. SEM Images of the Fe-N-C catalysts and of the silica template: a) silica template SBA-15, b) Fe-N-C^{NaOH+HCl}, c) Fe-N-C^{HF} and d) Fe-N-C^{Teflon}.

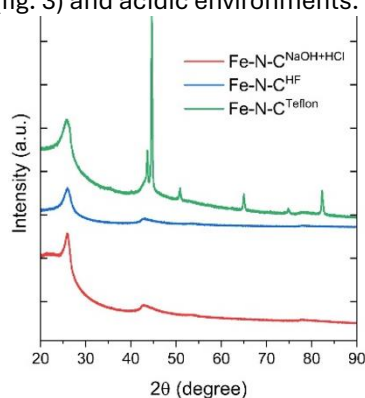


Fig. 2. XRD spectra of the Fe-N-C catalysts.

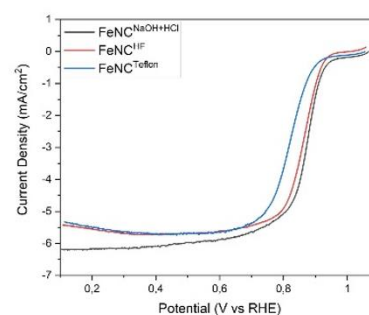


Fig. 3. ORR electrocatalytic activity on the samples in alkaline environments.

Among all the synthesis strategies here presented, FeNC^{NaOH+HCl} results as the most performant catalyst, with values of the onset (0.93 V) and halfwave potentials (0.87 V) are quite high and in agreement with literature expectations. By the four-electrode measurement (RRDE) it is also possible to understand the ORR mechanism, which mainly undergoes four-electrons reduction pathways, with a consequent low production of peroxide. In conclusion, we can announce that FeNC catalysts are a valid solution for ORR, offering a more cost-effective and sustainable alternative to platinum-based catalysts.