

Fe-N-C non-noble catalysts for applications in Fuel Cells and Metal Air Batteries - Abstract

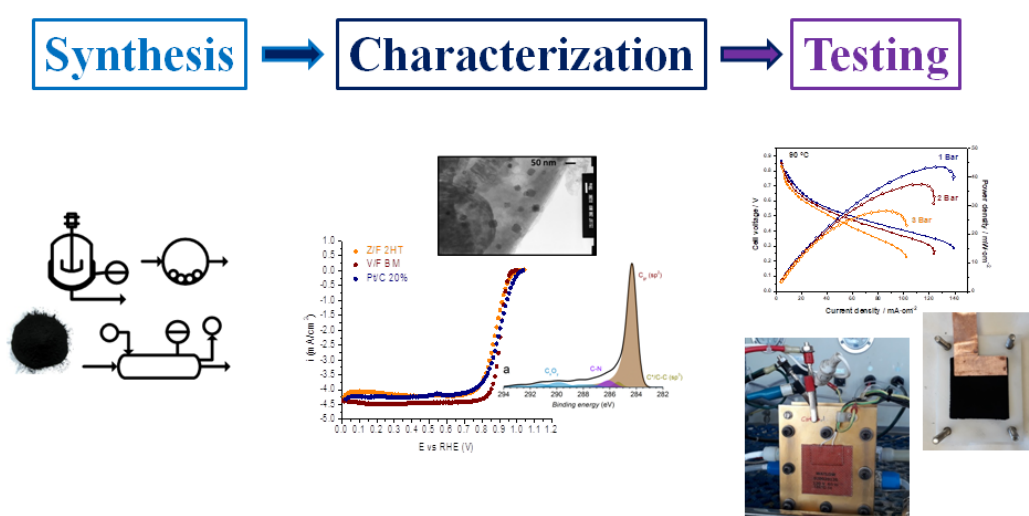
In this work of thesis, two non noble metal (NNM) catalysts active toward oxygen reduction reaction (ORR) were synthesized, optimized, characterized and finally tested in Direct Ethanol Fuel Cell (DEFC) and Metal Air Battery (MAB).

The catalysts were designed combining carbonaceous materials with iron and nitrogen precursors. The first catalyst, named Z/F 2HT, was obtained mixing the metal organic frameworks Basolite z1200 (Zif-8) with Fe-Phthalocyanine. The synthesis was performed using an autoclave step followed by two heat treatment (HT) at high temperature with intermediary acid leaching. The synthesis optimization was carried out following both the *design of experiment* method and the *one factor at one time* approach. The second catalyst, named V/F BM, was obtained mixing different amount of Vulcan XC 72 with Fe-Phthalocyanine using the mechanochemical synthesis through ball milling (BM) process. The synthesis optimization was carried out following the *one factor at one time approach*. Several heat treatments were evaluated as well.

Different electrochemical, chemical and surface analyses were carried out in order to investigate the properties and the difference between the two catalysts obtained after their synthesis processes. Specifically, the catalysts were analysed in RDE and RRDE configurations, in alkaline medium, in terms of stair case voltammetry, cyclic voltammetry, Tafel analysis, short load cycle durability test, ethanol tolerance, Koutecky Levich analysis, and H₂O₂ production as electrochemical evaluation. BET, SEM, XPS, and %Fe with ICP analysis as chemical physical analyses. A Pt/C commercial catalyst was used as a reference in the RDE/RRDE analyses. Since the characterization showed good results (half wave potential Z/F 2HT: 0.87V, V/F BM: 1.01 V, Pt/C: 1.01 V), the catalysts were further tested in electrochemical devices. The V/F BM catalyst showed better performance compared to the Z/F 2HT catalyst in terms of electrochemical activity and was studied for both DEFC and MAB applications. The Z/F 2HT material was tested only in MAB.

Pt/C and MnO₂/C were used respectively as DEFC and MAB commercial catalyst references. The experiments carried out in DEFC were promising: V/F

BM reached 70 mW cm^{-2} as maximum power density and $53 \text{ mW mg}_{\text{Pt}}^{-1}$ as mass specific power density. These values have the same order of magnitude of the best non noble metal catalysts reported in literature for DEFC. Concerning the durability, further improvement are required with the aim to understand if the performance loss are caused by the device or the catalyst. The application of the two catalysts in MAB demonstrated a different behaviour from the laboratory predictions. At lower discharge current density (1.6 mA cm^{-2}) the Z/F 2HT showed better results both in terms of durability and capacitance. At higher discharge current density (3.2 mA cm^{-2}) V/F BM catalyst showed the best performance. Both the Z/F 2HT and V/F BM catalysts showed closer but still lower electrochemical performance compared to the commercial MnO_2/C reference catalyst.



Graphical abstract