Electrocatalysts based on carbon materials and transition metals for their application in hydrogen production and use

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Objectives and novelty

This Doctoral Thesis was dedicated to the development of novel materials based on highly dispersed metals supported over N-doped carbon materials for their use as electrocatalysts for energy applications including hydrogen production, fuel cells and zinc-air batteries. The preparation of carbon nitride and activated carbon composites, coordinating highly dispersed metals like Cu or Fe, was explored conducting both experimental and computational studies to understand the behavior towards the oxygen reduction reaction (ORR). The addition of low amounts of Pd was optimized to boost not only the electrocatalytic activity towards other reactions but also the durability. Additionally, alternative carbon supports with potential superior stability (different boron-doped diamond powder materials) were explored and a novel procedure for producing biomass-derived electrocatalysts reducing the cost and environmental impact of the available procedures in literature was developed. The feasibility of the use of the biomass-derived materials forming membrane electrodes assemblies (MEAs) was confirmed by different studies on a 5 cm^2 cell during a stay in the *Institute of Advanced Technologies for Energy of the Italian National Research Council* (CNR-ITAE).

The novelty of this Thesis lies in the combination of advanced synthesis strategies, computational calculations (Density Functional Theory (DFT)) and verification in real working conditions to study the viability of the production of more efficient and stable electrocatalysts decreasing the production cost and environmental impact. The preparation procedure of the biomass-derived electrocatalysts led to a patent application and the publications related to the Thesis are listed below following the order of the chapters. These contributions open new possibilities for more sustainable electrocatalysts production for different energy applications, especially for the ORR process in direct methanol fuel cells and hydrogen evolution reaction (HER) in electroreforming cells. Finally, in the last chapter, the electrosynthesis of hydrogen peroxide is addressed for the first time by a metal tellurate-based material.

Results

The characterization of carbon nitride (C_3N_4)/activated carbon composites revealed that the presence of Fe leads to the formation of larger C_3N_4 domains, whereas Cu-containing counterparts exhibited well-distributed nanodomains, more similar to metal-free composites. The samples with a moderate content of C_3N_4 demonstrated high electrocatalytic performance, as they provided an optimal balance of surface metal active sites and textural properties. DFT calculations suggested that Cu-C_3N_4 sites possess superior catalytic properties in terms of activity and selectivity (Fig. 1), aligning with experimental findings. The properties of Pd nanoparticles were found to be dependent on the composition of the C_3N_4/C support, with highly dispersed Fe and especially Cu leading to smaller and more uniform Pd particle size distributions. This observation correlated with the higher stabilization energy predicted by DFT for an 8-atom Pd cluster with the support in presence of a second metal. Among Pd-containing materials, the best HER performance was observed in Pd/Cu-C3N4 sites, whereas the Pd/Fe-C_3N_4 composite showed the highest ORR/OER bifunctionality. This material was tested in a Zn-air battery, where it demonstrated performance comparable to a Pt/C + RuO_2 reference at low current densities.

A method was successfully developed to synthesize ORR electrocatalysts from biomass residues (schemed in Fig. 2(a)). The use of conventional activation agents such as H_3PO_4 or KOH was avoided by optimizing the content of Fe precursor (FeC_2O_4) to obtain adequate textural properties and excellent electrocatalytic performance. Electron microscopy studies, performed at the University of Cadiz thanks to an Integrated Infrastructure for Electron Microscopy of Materials (ELECMI) project, confirmed that a significant fraction of Fe formed small clusters likely coordinated with N, with the best ORR activity observed in catalysts containing approximately 5 wt.% of Fe (Fig. 2 (b,c)). The reproducibility of this method was confirmed by studying different biomass residues, with oceanic posidonia yielding the best performance.

In an anion-exchange direct methanol fuel cell (ADMFC) device, one of the electrocatalyst prepared by the above-mentioned method achieved a power density similar to that of a 40 wt.% Pt/C in a membrane electrode assembly (MEA). While the power density did not surpass that of state-of-the-art metal-nitrogen-carbon catalysts, its potential was confirmed by the low resistance, high methanol tolerance, and excellent stability. The performance and durability of Fe-N_x-C based materials as cathode catalysts in ADMFCs was found to be enhanced by the presence of low amounts of Pt nanoparticles (~2 wt. %). Structural modifications in Pt, as observed through X-ray diffraction (XRD), were linked to an

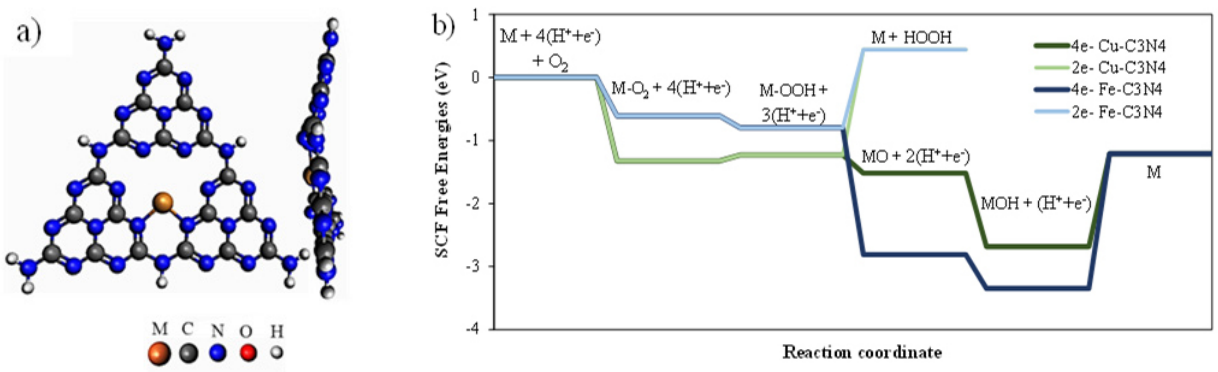

Figure 1. a) M-C3N4 optimized structure used and b) ORR free-energy diagrams (E = 0.8 V) showing 4- and 2-electrons pathways [1].

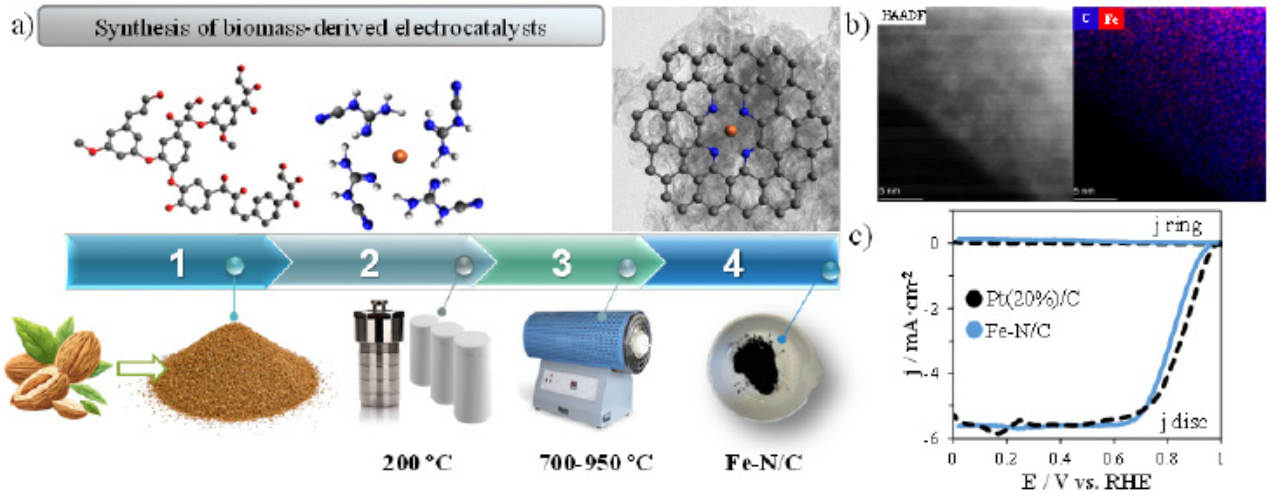

Figure 2. a) Scheme of the preparation procedure, b) characterization by scanning transmission electron microscopy with high-angle annular dark field imaging and energy dispersive X-ray spectroscopy, c) electrocatalytic activity towards ORR (1600 rpm, 0.1 M KOH solution) [5].

increased methanol tolerance. Pt-Fe based materials demonstrated superior durability compared to Pt-free materials, attributed to a synergistic effect preventing agglomeration and metal leaching. Additionally, a biomass-derived material with low Pt content was successfully applied as a cathode catalyst in an electroreforming cell, achieving a current at 60°C comparable to that of a Pt/C cathode containing 5-times higher Pt loading. A 30 h durability test at 125 mA cm^{-2} revealed significant degradation of the Pt/C catalyst mainly due to nanoparticle aggregation, whereas no significant modifications were detected for the biomass-derived catalyst. Finally, two metal tellurates were evaluated as ORR electrocatalysts for direct hydrogen peroxide electrosynthesis in alkaline media. Cu_3TeO_6 displayed instability at low potentials and mixed selectivity, whereas the Ni_3TeO_6-based composite exhibited excellent durability and selectivity. The addition of carbon black was necessary to enhance conductivity. However, excessive amounts negatively impacted selectivity, with the optimal Ni_2TeO_6:Vulcan ratio determined to be 2:1 by weight.

Conclusions

Carbon materials with different textural properties were prepared containing nitrogen heteroatoms such as nanodomains of C_3N_4 or N-functional groups on the carbon surface and several metallic phases including highly dispersed Cu and Fe, but also nanoparticles of Pd or Pt as second metallic phases. Some experimental studies were complemented with computational DFT modelling for a better understanding of the reactions and the nanoparticle-support interaction. ORR was the most studied electrochemical process during this Thesis, and some aspects like catalyst durability and methanol tolerance were especially addressed. Furthermore, the materials containing Pt and Pd were evaluated as HER electrocatalysts and Pd-based materials as bifunctional ORR/OER catalysts for a Zn-air battery air electrode. The feasibility of the biomass-derived materials production and application in an ADMFC device was confirmed by different studies in MEA conformation using real working conditions and long-term durability tests.

Acknowledgments

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