Hierarchical Electrocatalysts for the oxygen reduction reaction with a Graphene *"Core"* and a Carbon Nitride *"Shell"* exhibiting a Low Pt loading

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The worldwide energy system is currently undergoing a major transition towards a future where electrochemical energy conversion and storage (EECS) systems are becoming crucial. In this framework, proton exchange membrane fuel cells (PEMFCs) are particularly relevant due to their outstanding efficiency and compatibility with the environment [1]. The operation of PEMFCs is based on the conversion of the chemical energy associated with the oxidation of hydrogen into electrical energy. The oxygen reduction reaction (ORR), taking place at the PEMFC cathode, is one of the most critical bottlenecks in this process. The ORR is sluggish and it must be promoted by suitable electrocatalysts (ECs) to ensure that the PEMFC achieves a performance level compatible with the intended application [2]. The most effective ORR ECs for PEMFCs comprise active sites based on platinum, whose scarcity in Earth's crust might give rise to supply bottlenecks. Thus, the development of ECs that are high-performing, durable and comprise a low loading of platinum (giving so rise to *"Low-Pt ECs"*) is a major goal of PEMFC research. This contribution overviews the development of an innovative family of ORR ECs including a low loading of Pt and characterized by active sites located on the surface of sub-nanometric clusters (SNCs) where Pt is alloyed with a first-row transition metal (*e.g.*, Ni, Cu). The latter operates as a *"co-catalyst"*, significantly improving the intrinsic performance of the active sites in comparison with the Pt baseline [3]. The EC supports comprise a hierarchical graphene-based (H-GR) *"core"* covered by a carbon nitride (CN) *"shell"*. H-GR consists of highly defective graphene nanoplatelets and carbon black NPs [4] to promote mass and charge transport. The CN *"shell"* is decorated with C- and N-based *"coordination nests"*, stabilizing the SNCs and boosting the EC durability. Here is elucidated the interplay between the EC preparation parameters, the physicochemical properties, the electrochemical behavior and the performance in a single PEMFC tested under operating conditions.

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References

[1] B. Dunn et al., *Science*, 334 (2011) 928-935.
[2] I. Katsounaros et al., *Angew. Chem. Int. Ed.,* **53**, 102 (2014).
[2] V. Di Noto et al., *Electrochem. Soc. Interface,* 24 (2015) 59-64.
[3] V. Di Noto et al., *Patent application PCT/EP2017/084801,* 2017.