

Plurimetallic alloys bonded in carbon nitride “shells” supported on “cores” of conducting nanoparticles as electrocatalysts for the oxygen reduction reaction (ORR)

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Proton exchange membrane fuel cells (PEMFCs) are an advanced family of energy conversion devices characterized by a high efficiency and a low environmental impact. The electrochemical reactions involved in PEMFC operation must be promoted by suitable electrocatalysts to achieve a sufficient performance level. This issue is of particular relevance for the electrocatalysts meant to improve the kinetics of the oxygen reduction reaction (ORR) [1]. The ORR is sluggish, and even the best state-of-the-art electrocatalysts suffer from a variety of drawbacks including large overpotentials, a relatively poor durability and a high cost [2]. Indeed, the best performance is afforded by materials characterized by platinum nanoparticles supported on conductive carbons showing a large surface area [2].

Over the course of several years, our research group has devised and optimized a new and unique three-step protocol for the preparation of advanced ORR electrocatalysts. In the first step, a hybrid inorganic-organic precursor is synthesized; subsequently, the material undergoes a multi-step pyrolysis process; the final electrocatalyst is obtained after suitable chemical/electrochemical activation procedures [3]. This protocol proved extremely flexible, allowing a good control of the chemical composition and morphology of the electrocatalyst. In particular, active sites based on plurimetallic alloys of the PGM-X type (PGM → platinum-group metal: Pt, Pd...; X → other metal: Fe, Co, Ni, Rh...) are obtained easily. These systems may show an improved turnover frequency in comparison with pristine platinum nanoparticles. Furthermore, nitrogen atoms are introduced in the graphite-like support, giving so rise to a carbon nitride matrix. The latter is able to better coordinate and stabilize the alloy nanoparticles bearing the active sites, improving the performance and the tolerance of the electrocatalysts to oxidizing environments such as that found at the cathode of a PEMFC [4].

A major improvement in the performance of this family of ORR electrocatalysts is achieved as the starting precursors include suitable electron-conducting nanoparticles as “cores”. It is demonstrated that the final materials are characterized by an improved dispersion of the active sites in the “shell” of a nanoparticle “core-shell” morphology (see Fig. 1). With respect to the corresponding “bulk” electrocatalysts, an enhanced performance in single-cell configuration is obtained due to an easier mass transport of reagents and products [5]. Outstanding results are found using carbon black nanoparticles as the “core” (see Fig. 1). Other conducting

“cores” are also explored, including Ni and Cu nanoparticles. In this case, the optimal performance is reached only after an extensive electrochemical activation procedure. Very promising results may be achieved, significantly enhanced in comparison with the Pt/C reference both in terms of overpotential and selectivity in the 4-electron mechanism of the ORR (see Fig. 2).

REFERENCES

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FIGURES

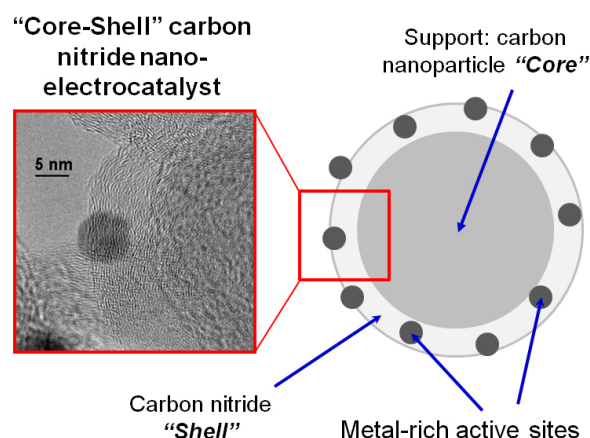


Figure 1. Morphology of “core-shell” carbon nitride nano-electrocatalysts obtained including conducting carbon nanoparticle “cores” in the precursor [5].

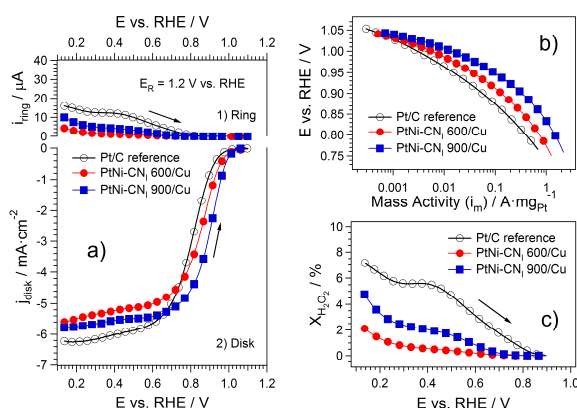


Figure 2. CV-TF-RRDE performance of PtNi-CN₁ T_f/Cu electrocatalysts in the ORR; T_f = 600 and 900°C. a) Positive-going sweeps determined on the electrode disk and ring; b) Tafel plots determined from the data shown in a) after removing the contributions due to mass-transport phenomena; c) Fraction of hydrogen peroxide evolved during the ORR by the prepared electrocatalysts as a function of the potential.

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