

## Graphene-supported Fe, Co, Ni carbon nitride electrocatalysts for the ORR in alkaline environment

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The development of advanced energy conversion systems characterized by a high efficiency and a low environmental impact is one of the most relevant targets of modern research [1]. As of today, important research efforts are devoted to low-temperature fuel cells (FCs) mounting an acid electrolyte, typically a proton-conducting membrane (e.g., Nafion®). To achieve a performance level compatible with current applications, these systems must adopt electrocatalysts (ECs) with a significant loading of platinum-group metals (PGMs). In conventional low-temperature FCs, most of the PGM loading is typically concentrated at the FC cathode to promote the poor kinetics of the oxygen reduction reaction (ORR), one of the major bottlenecks in FC operation.

Very recently, viable OH<sup>-</sup>-conducting membranes were developed [2], opening the possibility to devise efficient anion-exchange membrane fuel cells (AEMFCs). In these systems the ORR takes place in an alkaline environment; accordingly, AEMFCs can adopt "Pt-free" ORR ECs and still achieve a high performance level. In this work, new "Pt-free" ORR ECs are reported; the materials comprise a graphene support "core", which is covered by a carbon nitride "shell" coordinating the ORR active sites [3]. The proposed materials reap the benefits offered by graphene, including: (i) a high electrical conductivity, minimizing the ohmic losses; and (ii) a low microporosity, to facilitate the mass transport of reactants and products. The carbon nitride "shell" coordinates the bimetallic active sites, which include: (i) a 3d-"active metal" (i.e., Fe, Co, Ni), which bestows most of the ORR performance; and (ii) an oxophilic "co-catalyst" (Sn), which stabilizes the "active metal" and improves the ORR kinetics with a bifunctional mechanism.

The chemical composition of the ECs is determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and microanalysis; the thermal stability is studied by high-resolution thermogravimetry (HR-TG); the surface chemical composition is explicated by X-ray photoelectron spectroscopy (XPS); the morphology is elucidated in detail by high-resolution scanning electron microscopy (HR-SEM) and high-resolution transmission electron microscopy (HR-TEM); the porosity is inspected by nitrogen physisorption techniques; the structure is investigated by wide-angle X-ray diffraction (WAXD), electron diffraction and micro-Raman; finally, the ORR performance and mechanism are clarified by means of cyclic voltammetry with the thin-film rotating ring-disk electrode (CV-TF-RRDE) method. The results proved very promising, clearly showing the potential of this family of "Pt-free", "core-shell" graphene-supported ECs for application at the cathode of AEMFCs. In particular, CV-TF-RRDE measurements in an alkaline environment demonstrated that the best material exhibits an ORR overpotential ca.70 mV higher with respect to a 10 wt.% Pt/C reference.

### References

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