

“Pt-free” ORR Electrocatalysts comprising Graphene-Based “Cores” and Metal Carbon Nitride “Shells”

Vito Di Noto^{1,2}, Enrico Negro^{1,3}, Angeloclaudio Nale¹, Ketì Vezzù¹, Gioele Pagot^{1,3}

¹Section of Chemistry for the Technology (ChemTech), Department of Industrial Engineering, University of Padova, Via Marzolo 9, I-35131 Padova (PD), Italy

²Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali - INSTM, Via Marzolo 1, I-35131 Padova (PD), Italy

³Centro Studi di Economia e Tecnica dell’Energia Giorgio Levi Cases, Via Marzolo 9, I-35131 Padova (PD), Italy

Contact E-mail: vito.dinoto@unipd.it

One of the most relevant factors limiting the performance of proton-exchange membrane fuel cells (PEMFCs) is the large cathode overpotential, that is associated to the sluggishness of the oxygen reduction reaction (ORR). In conventional state-of-the-art PEMFCs the ORR is promoted by electrocatalysts (ECs) that include a very high loading of platinum-group metals in order to achieve performance and durability levels that are matching the requirements set by the applications. Indeed, Pt is the element that affords the best ORR kinetics in an acidic environment. This is a major shortcoming of today’s PEMFCs, whose large-scale rollout is hindered by the significant risk to incur in Pt supply bottlenecks [1].

This issue is addressed by developing ORR ECs that do not include platinum (“Pt-free” ECs). It is shown that the ORR can be effectively promoted by active sites that are based on a first-row transition metal (*e.g.*, Fe, Co and Ni), that is bound on the surface of the EC by coordination interactions mediated by C and N ligand atoms. It is also revealed that the EC performance is raised significantly by the addition of another element (*e.g.*, Sn) that acts as a “co-catalyst”. The ORR kinetics of such “Pt-free” ECs improves dramatically in an alkaline environment, where the adsorption of O₂ on the active sites is more facile. Finally, the performance and the durability of the “Pt-free” ECs are strongly affected by the chemical composition, structure and morphology of the support, that must minimize the ohmic drops and facilitate the mass transport phenomena.

In this framework, in principle graphene is a very attractive support for ORR ECs as it affords: (i) a very high specific area; (ii) an outstanding electron mobility; and (iii) a negligible microporosity. Hence, graphene is adopted as the main component of the support included in a several different families of “Pt-free” ORR ECs, whose development is overviewed in this work. All the ECs described here are obtained with the synthetic protocol devised in our laboratory [2], and are characterized by a “core-shell” morphology. In detail, the graphene-based support “core” is covered by a carbon nitride “shell”, which stabilizes the active sites in “coordination nests” based on C- and N- ligands.

The physicochemical properties of the proposed ECs (*e.g.*, chemical composition, morphology, porosity and structure) are correlated with the ORR performance determined both in “*ex-situ*” measurements carried out in half-cell configuration and in single fuel cell tested under operating conditions. It is elucidated the impact of: (i) the chemical composition of the active sites; (ii) the features of the support (*e.g.*, size of graphene sheets, presence of spacers); and (iii) the details of the post-synthesis treatments carried out on the ECs on the ORR overpotentials and reaction pathway as a function of the pH of the environment.

References

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