

## Atomically precise metal clusters for oxygen reduction reaction in alkaline media

Alberto Vertova, Roberto Dalla Pergola, Alessandro Minguzzi, Sandra Rondinini Dipartimento di Chimica – Università degli Studi di Milano Via Golgi 19 e-mail alberto.vertova@unimi.it

Global warming and the huge production of the greenhouse gases are very actual concerns. A new paradigm for energy production must be followed, and in this context the possibility to increase the usage of renewable energies and the development and research on new technologies for efficiency energy production and storage are very actual issues. Fuel cells and metal air batteries are possible solutions to the worldwide energy requirements, but, to date, the Oxygen Reduction Reactions (ORR) still remain a bottleneck for a wide spread and use of these technologies.

For this reason, in the last 50 years a huge amount of work has been done on this reaction, in term of understanding the possible reaction mechanisms of the process and of investigating new cathodic materials to reduce the overall overpotential

To date, platinum metal group, finely dispersed on suitable carbon support, are the best materials commercial available[1,2]. However, some important drawbacks are connected with the use of Pt as catalytic metal: i) high cost; ii) scarcity; iii) stability of micro- and nanoparticles on carbon support; iv) poisoning with CO[3]. Therefore, obtaining new catalytic materials able to improve the activity, selectivity, and durability of the ORR reactions is desirable.

In this context, we have synthetized different carbonyl Pt clusters, either belonging to the  ${\rm [Pt_{3n}(CO)_{6n}]^2}$  series (Chini-type clusters), or based on fcc close packed metal cores, to prepare nanostructured electrocatalyst, supported on black carbon (Vulcan XC72R®) powder, to be employed as positive pole in fuel cells and metal air batteries. The synthesis and physic o-chemical characterization will be briefly presented and discussed. The electrochemical characterization of composite electrocatalytic powders has been carried out using Rotating Ring Disk Electrode in order to investigate the reduction route: 4 or 2 electrons pathway.

The values of ORR onset potentials and limiting currents for these new Atomically precise metal clusters are very interesting, especially for  $[Pt_{15}(CO)_{30}]^2$  and  $[Pt_{24}(CO)_{30}]^2$  which exhibits higher limiting currents than a commercial Pt-loaded carbon powder, despite the lower amount of noble metal. Moreover, these powder show a very low production of H2O2, thus indicating a preferential route for 4-electrons pathway reduction reaction. The results are presented in term of specific activity and mass activity.

- 1. Cao, M., Wu, D. & Cao, R. Recent Advances in the Stabilization of Platinum Electrocatalysts for Fuel-Cell Reactions. *ChemCatChem* **6**, 26–45 (2014).
- 2. Banham, D. & Ye, S. Current Status and Future Development of Catalyst Materials and Catalyst Layers for Proton Exchange Membrane Fuel Cells: An Industrial Perspective. *ACS Energy Lett.* **2**, 629–638 (2017).
- 3. Zhang, Y. *et al.* One-step synthesis of an octahedral  $Mn_3O_4/rGO$  composite for use as an electrocatalyst in the oxygen reduction reaction. *J. Solid State Electrochem.* (2018). doi:10.1007/s10008-018-3902-6