## Design and development of new nanostructures as efficient catalyst toward ORR Giulia Massaglia, PhD

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Energy challenges and environmental problems due to the large use of fossil fuels are driving the demand for the development of new approaches for renewable energy conversion and electrochemical storage. Among the currently available techniques, Polymeric Electrolyte Membrane Fuel Cells (PEM-FCs) shine as an environmental-friendly and versatile low temperature FC technology, able to combine simplicity and reliability to ease of scaling up. Nonetheless, PEM-FCs suffer of great limitations to their need of expensive polymeric electrolytes and catalysts at both the electrodes, resulting in high costs that are still limiting their penetration into the energy market. The oxygen reduction reaction (ORR) occurring at the cathode, has a relatively slow kinetics usually limiting the final efficiency for these electrochemical devices. Metal noble catalysts and especially platinum (Pt), are currently the best performing class of catalysts for direct ORR, able to overcome its slow kinetics. However, since these materials result to be expensive and not abundant in nature, their use must be limited and the development of new electro-catalysts with high catalytic activity, longer durability and low economic impact, is highly recommended.

In this scenario, novel Pt-free catalysts in the form of electrospun nanofibers are receiving a special attention for the ORR. Electrospinning is a unique and versatile electro-hydrodynamic process able to organize polymer-based solutions into nanofibers mat. Electrospun nanofibers can be defined as the conjunction point between the nanoscale world and the macroscopic one, thanks to their diameters, in the range of some tens of nanometers, and their length, which can reach up to some kilometers. The application of nanofibers is widespread in all sectors from medicine to environmental sciences, and during the last decade they gained a pivotal role also in devices for energy conversion and storage, especially to design and synthesis catalysts thanks to their intrinsic properties, such as high porosity, large surface area to volume ratio, excellent mass transportation and simply tunable composition.

During the last years we focused our research activity on the development of Pt-free nanomaterials, demonstrating that electrospinning can play a crucial role for further development in this area of catalysis. We especially investigated two main class of catalytic nanomaterials: i) carbon-based nanomaterials; ii) transition metals nanocompounds. We demonstrated that carbon-based nanofibers, intrinsically doped with heteroatoms, like nitrogen, can play a crucial role as a substitute to platinum [1]. With the main aim to modify the distribution of the N-doping sites into carbon-based nanofibers, tuning the defects content to improve the ORR catalytic activity of these nanomaterials, we successfully demonstrated that plasma treatments are an effective method to modify the distribution of the N-doping sites [2]. Finally, for what it concerns the employment of transition metals oxides we focused our interest on nanostructured manganese oxides [3-5], and we especially developed a new electrospinning on electrode (EoE) assembly as a simple and efficient electrospinning-based binder-free method to selectively deposit Mn<sub>3</sub>O<sub>4</sub> nanomaterials onto cathode electrode [6].

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