Design of Aerogel-based Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells

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Great advancements have been made in the past couple of decades in the development of platinum group metal-free (PGM-free) oxygen reduction reaction (ORR) catalysts based on earth-abundant elements such as nitrogen, carbon, and first-row transition metals (usually Fe or Co, but also Cu and Mn). This work has been mostly inspired by biological systems where some of the catalytic centres are composed of complexes of metallo-porphyrins and phthalocyanines. These molecular catalysts show fair, but not exceptional ORR activity and stability. In order to increase the performance of transition-metal complexes, a new class of high temperature-treated (HT-treated) catalysts, composed of the same elements, i.e., a transition metal, carbon and nitrogen, has been developed. Although some improvements were made, the performance of HT-PGM-free ORR catalysts remains inferior to PGM catalysts, calling for further improvements in order to make them a viable alternative to the state-of-the-art materials. One such direction is the increase of the active site density, and catalyst utilization to mitigate their intrinsically low turnover frequency (TOF).

In this work, we designed, synthesized, and characterized ORR catalysts based on iron and/or copper, carbon and nitrogen in a well-defined, high surface-area covalent framework (COF) of aerogels. Aerogels are ultralight, porous materials, with ultra-low density, and high void volume (> 97%), also known for their unique physicochemical properties such as high porosity, controllable pore size and surface area, just to name a few. The variety of precursors used for aerogel synthesis makes them promising candidates for a wide range of applications in catalysis, capacitors, insulators, absorbents, and many more. In the context of electrocatalysis of fuel cells' reactions, carbon-aerogels have been mostly used so far as catalysts' supports for PGM and PGM-free catalysts.

In their inorganic form, aerogels can have ultra-high catalytic site density, high surface area, and tuneable physical and chemical structures - all very important features for a heterogeneous catalyst. In this talk, I will discuss the synthesis and electrocatalytic properties of several transition metal-based aerogels developed in my research group. For example, at the beginning of our work on this topic, we synthesized an aerogel based on 5,10,15,20-(tetra-4-aminophenyl)porphyrin (TAPP) and Fe(II), which was later heat-treated at 600°C to enhance its electronic conductivity and catalytic activity while preserving its macro-structure. The resulting material has a very high concentration of atomically dispersed catalytic sites ($4.01 \cdot 10^{19}$ sites cm^{-3}), capable of catalyzing the ORR in alkaline solution very well (E_{onset} = 0.93 V vs. RHE, TOF = 0.2 e^{-} $site^{-1}$ s^{-1} at 0.8 V vs. RHE). I will present the work we conducted on this topic and include some of our most recent unpublished results with bi-metallic complexes which show exceptional performance.