Nano-structured and hierarchically structured materials play a vital role in electrochemical power source technologies: batteries, super capacitors and fuel cells. They are becoming increasingly important in electrochemical synthesis technologies such as electrolysis, photolysis, CO2 electro-reduction and production of value added chemicals. Nano-materials contribute to the enhancement of the catalytic properties of the electrodes, dramatically improve interconnectivity of porous matrixes and revolutionize mass-transport characteristics on micro- and meso-scale. Their main role is in enabling the display of phases of greater catalytic activity, stabilizing "unusual" surface moieties that are not displayed in quantities in bulk phases and in facilitating transport phenomena and through this increasing of volumetric (and in some cases, gravimetric) power density, provide for higher energy density and facilitate increased rate of drain. Detailed understanding of these processes allows even broader exploration of nano-materials for energy conversion and storage. Structural properties of these materials are making possible new design solutions and provoke a new stage in power source systems engineering. All these will bring substantial benefit if manufacturing of such materials could meet the demand in volume, performance and reproducibility.

Non-PGM catalysts have been extensively developed for both Proton Exchange Membrane (PEM) and Alkaline Exchange Membrane (AEM) fuel cells both aiming automotive applications. In this overview we will address the critical challenges that UNM team has faced on the way to practical application of such catalysts.

UNM has developed the Sacrificial Support Method (SSM) as a main approach for templated synthesis of hierarchically structured electrocatalysts materials. In this method the catalysts precursors are being absorbed on, impregnated within or mechanically mixed with the support (usually mono-dispersed or meso-structured structured silica), thermally processed (pyrolyzed) and then the silica support is removed by etching (in KOH or HF) to live the open frame structure of a “self-supported” material that consists of the catalysts only (see Fig. 1).

![Fig. 1: Schematic of a “open-frame” structured electrocatalyst in contrast with the traditional decorated powder material design.](image)

This presentation brings examples from two materials synthesis platforms: aerosol processing in a format of spray pyrolysis\(^1,2\) and colloidal approach based on sol-gel templating of micro-emulsions.\(^3,4\) Both approaches have been used at UNM over the last decade to design electrocatalyst powders with varied chemical structure and desired morphology for fuel cell and related applications. The spray-based process results in formation of unique spherical, micron-sized aggregates consisting of sub-micron electrocatalyst particles where the nanometer sized active phases are highly dispersed. Examples include platinum group metals (PGM) and metal alloys; metal oxides, composite and non-noble or graphene metal electrocatalysts. Microemulsion-derived materials have three levels of morphology control: nanopores derived from micellar structure of the surfactant used, mesopores templated on the microemulsion droplets and macrostructured particles resulting from sheer mixing. We have developed these two approaches to produce not only traditional electrocatalysts (PGM and their alloys supported as decorative phase on carbon blacks) but also a whole new set of reactive oxide and conductive oxide materials that serve as co-catalysts or non-carbonaceous supports.\(^5,6\)

Synthesis of non-platinum electrocatalysts based on transition metals and N-containing carbonaceous materials obtained by both methods will be discussed as well.\(^7,12\) Such hierarchical structures are advantageous in enhancement of the fuel cell performance since they correspond to the different levels of transport in the corrugated electrode matrixes. Fig. 2 illustrates the SSM when it is applied to synthesis on Non-PGM catalysts.

![Fig. 2: Sacrificial Support Method for templated synthesis of Non-PGM electrocatalyst of Transition Metal-Nitrogen-Carbon class.](image)

A wide variety of materials can be made by these methods in which not only the composition but also the microstructure can be varied. It is the combination of these attributes - control over microstructure at a number of different length scales and composition, simultaneously - that is extremely important to the performance of the electrocatalyst materials in a fuel cells. This paper will bring examples of successful practical applications of our materials in automotive technologies using both Polymer Electrolyte (PEMFC) and Alkaline Membrane (AMFC) Fuel Cells with gaseous and liquid fuels.\(^13,14\)