

## Catalysts for Electrooxidation of Ethanol and Other Biofuels

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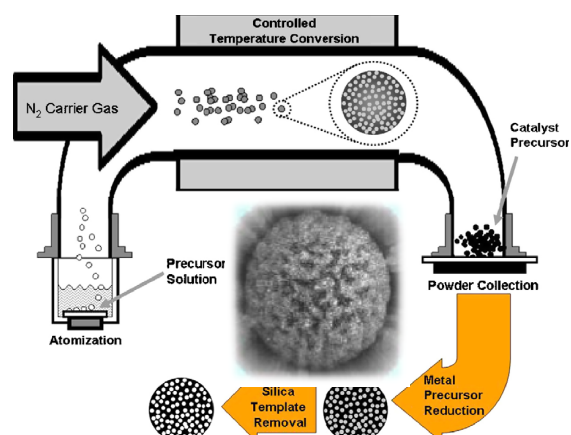
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Direct alcohol fuel cells are a viable alternative to the traditional hydrogen PEM fuel cell. Fuel versatility, integration with existing distribution networks, and increased safety when handling these fuels increases their appeal for portable power applications. In order to maximize their utility, the liquid fuel must be fully oxidized to CO<sub>2</sub> so as to harvest the full amount of energy. Methanol and ethanol are widely researched as potential fuels to power these devices, but methanol is a toxic substance, and ethanol lower energy density than other liquids such as gasoline or glucose. It is however produced as a major biofuel along with some other polyols (such as glycerol) and presents a case for integration with fuel cell technology. Oxidation of complex fuels is difficult to realize, due to difficulty in breaking carbon-carbon bonding and poisoning of the catalysts by oxidative byproducts. In order to achieve the highest efficiency, an anode needs to be engineered in such a way as to maximize activity while minimizing poisoning effects of reaction byproducts. We have engineered a series anode catalysts, that use platinum group metals (Pt or Pd) in combination with more oxophilic metal (Cu, Zn, Pb, Sn, La) or its oxide, to form bi- and tri-metallic nano-composites that is capable of deep oxidation of ethanol, ethylene glycol and glycerol in alkaline media with little evidence of CO poisoning.

All catalysts presented in this work were synthesized using a sacrificial silica support method, which was developed in our research group. Appropriate amounts of metal precursors (platinum or palladium nitrate, lead or tin nitrate etc) were deposited on the surface of fumed silica Cab-O-Sil® EH-5 (surface area ~380 m<sup>2</sup> g<sup>-1</sup>). The composite materials were chemically reduced using solution NaBH<sub>4</sub> or thermally reduced in H<sub>2</sub> atmosphere. After reduction, the fumed silica was removed by etching in KOH solution, and washed appropriately.

All these materials were demonstrated to be scaled up by using spray pyrolysis (see Fig. 1), a semi-continuous aerosol synthesis method in which the precursor salts and the silica powder are suspended in solution, this solution is atomized into aerosol and the droplets are passed through a hot-wall furnace in a laminar flow of carrier gas. The thermochemical processes happen in the droplet during its residence time in the furnace. The resulting powder is collected, etched to remove the silica in KOH and post-processed in hydrogen atmosphere to reduce to metal/oxide composite. The morphology of such powder is spheroidal secondary particles (~ 1 μm diameter) resulting from the materials contained in each individual aerosol droplet. Each spheroid has internal porosity templated by the sacrificial silica support. Thus, the materials synthesized and scaled up have hierarchical porosity (see the insert in Fig. 1).



**Figure 1.** Schematic of the spray pyrolysis synthesis of hierarchically structured templated PGM-based multi-metallic electrocatalysts. Insert: SEM image of the catalyst

The catalysts were evaluated for electrooxidation of ethanol, ethylene glycol and glycerol using in situ FTIR-spectro-electrochemical cell. Catalytic activity for alcohols oxidation was measured in alkaline media using the RDE method. The catalysts were comprehensively characterized by BET, SEM, TEM, XRD and XPS. The spectra for different catalysts compositions were processed by Multivariate Spectral Analysis and were correlated with electrochemical performance.

This paper will discuss the results obtained with the three generations of catalysis materials and will provide comparative study in structure-to-property relationships.

**Acknowledgement:** This work was supported DOE-BES EPSCoR Implementation Program. The main goal of the research program is to provide an enabling materials set for bridging mass-produced biofuels such as ethanol with fuel cell technology. Two intertwining pathways have been explored: 1) ethanol reforming to produce hydrogen, a feed for a H<sub>2</sub>/O<sub>2</sub> fuel cell and 2) direct electrochemical oxidation of ethanol. The first path involves the study of aqueous phase ethanol reforming and identifying the limiting step of oxidation of ethanol in presence of water. The results of this study are being applied to a rational design of an electrocatalyst for direct ethanol fuel cells.

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