

Electrocatalyst Design for an Elevated Temperature Proton Exchange Membrane Direct Ethanol Fuel Cell  
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Access to a liquid fuel with a high volumetric energy density would offer major advantages to the proton exchange membrane (PEM) fuel cell (FC). One avenue to such a fuel is the utilization of carbon-carbon bond containing substrates, since the conversion of such materials to carbon dioxide and water represents a major energy release avenue. This is illustrated in the table below which shows that while hydrogen, the classic PEM fuel has an excellent energy density, it has (even in the liquid state) a poor volumetric density. Methanol, although it undergoes a 6-electron oxidation to carbon dioxide only contains C-H bonds, and thus, offers fairly low volumetric and gravimetric energy densities. However, ethanol with a single C-C bond yields a volumetric energy density that is ~66% of the energy density found in gasoline.

Table: Comparison of Energy Densities of Potential Fuels Evaluating the Impact of a C-C Bond Containing Fuel

Fuel	Gravimetric Energy Density	Volumetric Energy Density
Liquid H <sub>2</sub>	120 MJ/kg,	9 MJ/L
Methanol	20 MJ/kg,	16 MJ/L
Ethanol	27 MJ/kg,	21 MJ/L
Gasoline	44 MJ/kg,	31 MJ/L

Unfortunately, while effective anode electrocatalyst are available for hydrogen and methanol based PEM fuel cells, a direct ethanol catalyst has not been identified. The limitation appears to be the ability of the catalyst to split the carbon-carbon bond. In the case of ethanol, a catalyst that could efficiently convert the substrate to carbon dioxide would produce a fuel cycle that delivered 12e<sup>-</sup> (at an open circuit potential of ~1.14V) Of equal importance, once such a catalyst is available then all higher order alcohols become potential fuels, dramatically increasing the available volumetric energy density.

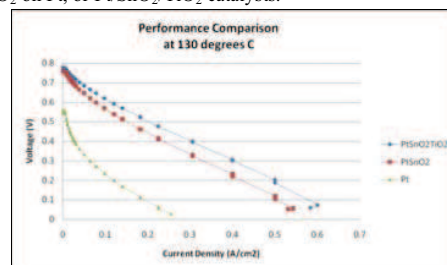
It has previously been noted that the Pt<sub>3</sub>Sn intermetallic has limited catalytic activity for the oxidation of aqueous ethanol to carbon dioxide under standard PEMFC thermal conditions. However, we have found that carbon dioxide is a minor product in this system with acetaldehyde (2e<sup>-</sup> oxidation) and acetic acid (4e<sup>-</sup> oxidation) being the major products.<sup>1</sup> As expected for these products (that have an intact C-C bond), the voltage-current response the fuel cell using a Pt based oxygen electrode is quite poor. Further, consideration of this system also suggests that the proposed catalyst alloy may not be the active catalyst since this material should be thermodynamically unstable under the potential conditions associated with a direct ethanol fuel cell, degrading to platinum and SnO<sub>2</sub>. Thus, it is far more likely that the actual catalytic species in this cell is a Pt/SnO<sub>2</sub> composite.

To investigate this system we have used a polyol synthesis procedures developed initially by Sun et. al. to directly produce a Pt/SnO<sub>2</sub> catalyst,<sup>2</sup> but have modified the synthesis by exchanging the standard heating procedures with a microwave treatment. This new synthesis produces a very homogeneous dispersion of

nanoparticles. While the synthesized material is found to be an improvement over the Pt<sub>3</sub>Sn catalyst, it is still relatively inefficient at oxidizing aqueous ethanol to carbon dioxide. Sun initially characterized this catalyst as platinum nanoparticles on a SnO<sub>2</sub> support.<sup>2</sup> However, high resolution transition electron microscope (HRTEM) studies in our lab using single particle elemental analysis and electron diffraction suggest that the active catalyst is a platinum nanoparticle that is partially shrouded in an incomplete SnO<sub>2</sub> surface layer.<sup>1</sup> We find that further improvement in the catalytic activity of this material can be obtained by both adding a TiO<sub>2</sub> oxide phase and carefully controlling the dispersion of the catalyst on the carbon support material.

Elevation of the PEMFC operating temperature is also advantageous as shown in the Figure below which several voltage-current responses at 130°C. For the Pt/SnO<sub>2</sub> system shown, 12% of the product is found to be carbon dioxide. While this is a significant improvement, it falls short of the goal. However, we also find that another 12% of the product is methanol. Thus, the catalyst provides about 25% conversion efficiency to C<sub>1</sub> products; a clear improvement in C-C bond breaking efficacy.

Figure: Voltage-Current Response for Direct Ethanol Single Cells Operating at 130°C and Utilizing Either Pt, SnO<sub>2</sub> on Pt, or Pt/SnO<sub>2</sub>/TiO<sub>2</sub> catalysts.



Available data hints that the ability to break the C-C bond may hinge on having a Lewis acid that can interact with the alcohol function along with a charge transfer catalyst that directly interacts with the C-C moiety. To explore this hypothesis we have produced a wide variety of metal oxide on platinum or palladium nanoparticles and surveyed their catalytic potential using cyclic voltammetry at a glassy carbon electrode. Promising systems are then evaluated in a PEMFC as a function of temperature, with runtime products determined by GC.

The analysis of these systems will be presented and discussed with the two-fold goal of identifying systems of pragmatic interest, and determining mechanisms of electrocatalytic charge transfer.

#### References

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- Jiang, L. H.; Sun, G. Q.; Sun, S. G.; Liu, J. G.; Tang, S. H.; Li, H. Q.; Zhou, B.; Xin, Q., *Structure and Chemical Composition of Supported Pt-Sn Electrocatalysts for Ethanol Oxidation*. Electrochim. Acta, 2005, **50**(27): 5384-5389.