

Ethanol Oxidation and Beyond: Trends in Alternative Fuel Oxidation Schemes and Progress Towards the Complete Oxidation of Higher Energy Density Fuels

Shelley D. Minteer

USTAR Professor of Chemistry and Materials
Science and Engineering
The University of Utah
Salt Lake City, UT 84112, USA
minteer@chem.utah.edu

The appeal of solar-fuels and biofuels are many fold: they offer independence from foreign petroleum, an effective means of utilizing solar energy, and most pertinently, a means of mitigating atmospheric CO₂. (1) Solar energy utilization is a hierarchy of capture, conversion, and storage of energy. Plants have done this over millennia *via* photosynthesis. This is a template that much research looks to mimic and improve upon. However, the efficient utilization of solar energy stored chemically as solar-fuels is a key component in this cycle.

A main argument against the use of biofuels derived naturally from biomass and fermentation is that this process is inefficient (~1 %), and it does not offset CO₂; i.e., biofuel utilization is not a means of carbon sequestration. However, when utilized efficiently through electrochemical means it can be.

The paper will talk about more efficient oxidation of ethanol in biofuel cells and alkaline fuel cells. This work is focused on improving the complete catalysis of ethanol oxidation—utilizing enzyme cascades at bioanodes and non-precious metal based catalysts in alkaline systems.

Many biofuel cells rely on immobilized microbes or mitochondria for fuel oxidation at bioanodes. These systems are capable of complete oxidation (i.e., alcohol to CO₂). However, these systems suffer from low catalyst loadings and interfacial issues associated with biological membranes. Alternatively, enzyme catalyzed biofuel cells have higher catalyst loadings in bioanodes, as they do not contain the extra cellular components, nor are they hindered by the poor electronics of cellular membranes. Traditionally, enzyme catalyzed biofuel cells relied on a single enzyme, alcohol dehydrogenase. However, a single enzyme system produces only 2 electrons upon oxidation and an aldehyde product. Multi-enzyme cascades (2, 3) or bioconjugated enzyme metabolons (4, 5) are needed for this process. Research by our group has shown that cascades can completely oxidize ethanol to CO₂. Figure 1 emphasizes the

effect of multiple-enzyme cascades for the NAD⁺ dependent oxidation of ethanol. This enzymatic cascade will be compared to the use of DNA-nickel electrodeposited catalysts for ethanol oxidation and traditional electrodeposited catalysts for ethanol oxidation.

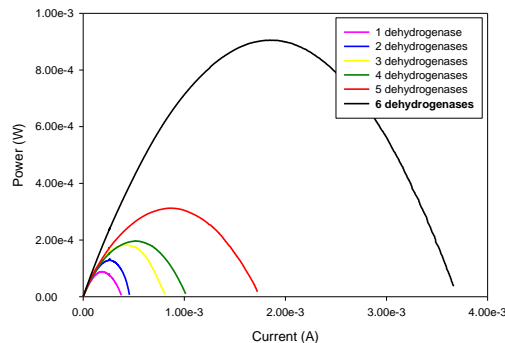


Figure 1. Representative power curves for the oxidation of 100mM ethanol.

References:

1. N. S. Lewis and D. G. Nocera, *PNAS*, **103**, 15729 (2006).
2. P. K. Addo, R. L. Arechederra and S. D. Minteer, *Electroanalysis*, **22**, 807 (2010).
3. D. Sokic-Lazic and S. D. Minteer, *Electrochemical and Solid-State Letters*, **12**, F26 (2009).
4. M. J. Moehlenbrock, T. K. Toby, L. N. Pelster and S. D. Minteer, *ChemCatChem*, **3**, 561 (2011).
5. M. J. Moehlenbrock, T. K. Toby, A. Waheed and S. D. Minteer, *Journal of the American Chemical Society*, **132**, 6288 (2010).