

## NADH Regeneration for Use in Bioelectrofuels Production

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Solar energy holds great promise as a renewable resource that doesn't produce carbon dioxide. It can only be collected for a limited portion of the day; however, so in order for it to become a feasible alternative to fossil fuels an efficient way to store that energy must be developed. Even the simplest organic fuels have much higher energy densities than batteries so creating a pathway to convert solar energy into chemical energy is a necessary step in developing solar energy.

Looking to nature provides an example of such a pathway in the form of photosynthesis. Photosynthesis consists of a set of light reactions that capture light and store the energy temporarily in ATP and NAD(P)H. This energy is then used in the Calvin Cycle in order to fix carbon dioxide and produce sugars. Because of its ability to fix carbon dioxide at ambient temperatures and concentrations, the Calvin Cycle and other bioelectrofuel production pathways are being investigated as potential pathways.

The nicotinamide adenine dinucleotide (phosphate) (NAD(P)H) cofactor is utilized in the Calvin Cycle as a reducing agent to produce glyceraldehyde-3-phosphate (G3P) from 1,3-bisphospho glycerate. Because it is expensive and consumed in stoichiometric amounts, it is important to regenerate the reduced form of the cofactor. The electrochemical reduction of NAD(P) to NAD(P)H is favorable as a regeneration technique, because it allows for the monitoring of the entire Calvin Cycle or other bioelectrofuel production pathways electrochemically.

Reduction of NAD(P) on a bare electrode surface results in the dimerization of the cofactor which renders it inactive enzymatically. In order to overcome this problem several surface modifications have been developed (1-5). Electro-polymerized neutral red was first investigated as a potential catalyst because previous studies had shown that it was capable of carrying out NAD(P) reduction at smaller overpotentials than are required on a bare electrode surface (5). Numerous attempts showed minimal catalytic effect. Additionally the polymer didn't exhibit sufficient stability for use in large scale regeneration of NAD(P)H.

Another set of electrode modifications that have been investigated for NAD(P) reduction are transition metal catalysts. Specifically, transition metals such as ruthenium and platinum which catalyze hydrogen evolution have been utilized as an effective way to avoid the formation of NAD(P) dimers. Dimers form because the reduction of NAD(P) is a two electron process and the first electron transfer produces a radical form of NAD(P) which can then bind with another NAD(P) radical on the electrode surface. By increasing the surface concentration of protons, it becomes more likely for NAD(P) molecules to react with a proton and form NAD(P)H instead of dimerizing with another NAD(P) radical. This strategy has indeed proven to be effective has been used to produce NAD(P)H that is enzymatically

active for use in a variety of bioelectrofuel production systems, as shown in Figure 1. Those systems will be compared in this talk.

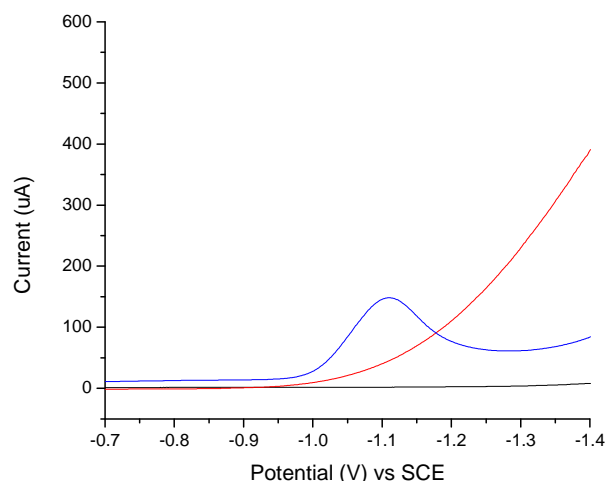


Figure 1. Representative voltammograms of hydrogen evolution and NAD(P) reduction on a ruthenium nanoparticle-modified surface. Glassy carbon that has been modified with ruthenium nanoparticles (red) catalyzes hydrogen evolution at lower potentials than bare glassy carbon (black). When NAD(P) is present (blue, 8mM) the increase in surface proton concentration leads to NAD(P) production instead of dimerization.

### References

1. Karyakin, A.A. Ivanova Y.N. Karyankina, E.E. *Electrochemical Comm.*, 5 (2003) 677
2. Rahman, G. et al. *Int. J. Electrochem. Sci.*, 6 (2011) 2789 - 2797
3. Man, F. Omanovic, S. *J. of Electroanalytical Chem.* 568 (2004) 301-313.
4. Walcarius A. et al. *Bioelectrochemistry* 82 (2011) 46-54.
5. Arechederra M. N., Addo P.K., Minteer S.D. *Electrochimica Acta* 56 (2011) 1585-1590