Synthesis of Biofuels on Bioelectrodes

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**Objective**
This research program explores the opportunities and bottlenecks of electrosynthesis, a technology that uses microorganisms to produce transportation fuel from electrical energy and atmospheric CO₂. The fundamental science encompasses microbial communities, their interaction with electrodes and the processes that allow efficient electron uptake, transfer and synthesis of fuels and fuel precursors such as methane, acetic acid and hydrogen. Understanding the interactions of microbes, and how their metabolic interactions are controlled, is an emerging field that is relevant for bioenergy as well as bioremediation, human health and ecosystem management.

**Background**
Petroleum and other fossil hydrocarbons are primarily used as energy sources for liquid (transportation) fuels and as raw materials to produce commercially valuable chemicals. These uses represent the largest anthropogenic contribution to atmospheric CO₂ and global warming. To reduce or eliminate this net release of CO₂, new approaches are urgently needed that connect electrical energy to the infrastructure advantages of hydrocarbon fuels and chemical precursors.

In nature, some microorganisms are capable of transferring cellular electrons to insoluble extracellular compounds, in particular to iron-oxide mineral surfaces, such as in hematite or goethite. This mechanism is a key feature of microbial fuel cells (MFCs), where the anode serves as the electron acceptor, and the cathode is oxidized typically by molecular oxygen. Microbes can also uptake low-potential electrons directly or indirectly from a cathode (Figure 1) to drive catabolic processes.

This project focuses on the microbial synthesis of methane, acetate and other hydrocarbons that can be easily separated from a bioreactor and used as carbon-neutral fuels or precursors.

![Figure 1: Excess electrons from carbon-neutral energy sources can be used by microbes to drive the reduction of atmospheric CO₂ and synthesize biofuels, such as methane.](image)

Specific reduction-oxidation (redox) enzymes, including hydrogenases and diaphorases, play an important role in mediating reductive reactions at the cathode (Figure 2). A cathodic fermentation process will be developed that feeds molecular hydrogen (H₂) to microorganisms for CO₂ fixation. The fixed CO₂ will be used to produce precursors of biofuels, such as acetate. This research will advance our fundamental understanding of low-potential redox enzymes, including hydrogenases,
and the molecular pathways of electron transfer within the enzymes. Moreover, the research will lead to the development of novel ways to engineer microbial communities for the production of biofuels.

**Figure 2:** Examples of enzymes (e.g., hydrogenase and diaphorase) and redox processes involved in microbial electrosynthesis. Key: e⁻ (electrons), H (hydrogen), Fe-S (iron sulfide), Ni-Fe (nickel-iron), FMN (biomolecule), NAD(P)H (coenzyme).

**Approach**

The initial research has focused on specific bacteria, such as *Cupriavidus necator* H16 and *Shewanella oneidensis*, which are known to metabolize electrons.

Using *C. necator* H16, the research team demonstrated for the first time the direct uptake and metabolism of electrons from the surface of a cathode. The data showed that *C. necator* H16 uses cathodic electrons during the metabolism of oxygen and nitrate. This important finding suggests that *C. necator* can be used as a platform for microbial electrosynthesis. Previous studies have shown that the hydrogenase enzyme of *C. necator* H16 can be used to coat an electrode to consume hydrogen and produce a current. If the electrons from the cathode can be channeled into respiration, then the energy that is generated could be used to drive other cellular processes, such as carbon dioxide fixation. Data obtained in the experiments with *S. oneidensis* indicate that this microbe might also be a very useful and effective.

**References**


