GCEP

Global Climate & Energy Project

STANFORD UNIVERSITY

Designing Metal Catalysts for Electrochemical Conversion of CO_2 and CO to Fuels and Chemicals

Investigators

Thomas F. Jaramillo, Department of Chemical Engineering, Stanford University; Jens K. Nørskov, Departments of Chemical Engineering, Stanford University, and of Photon Science, SLAC National Accelerator Laboratory; and Anders Nilsson, Department of Photon Science, SLAC National Accelerator Laboratory

Objective

The main goal of this research is to develop catalysts that can convert carbon dioxide (CO_2) and carbon monoxide (CO) into hydrocarbons and alcohols that can be used as fuels and chemicals. The project could ultimately lead to the coupling of renewable energy resources, such as wind and solar, to the production of fuels and chemicals through electrocatalytic reduction (Figure 1).

Background

Global demand for hydrocarbons and ethanol is huge, with annual production rates on the order of 10^{13} kg/yr [1]. On average, each person on Earth accounts for approximately 1,000 kg of production per year. Hydrocarbons and alcohols are conventionally derived from fossil sources or other feedstock that generate greenhouse gas emissions. Thus, finding renewable pathways to produce these molecules will become necessary. Such pathways will likely involve the reduction of CO_2 or CO by catalysts.

The CO_2 reduction reaction (CO_2RR) has been studied experimentally for some time and remains a notoriously difficult reaction to catalyze. The first major breakthrough came in 1985 with the discovery that methane and ethylene were the primary products on a copper metal electrode [2]. CO is believed to be an important intermediate in the reduction of CO_2. Studies have shown that how strongly a catalyst binds CO determines what products are made. Metals that bind CO strongly allow other reactions, such as hydrogen (H_2) production from water reduction, to outcompete the CO_2RR, resulting in fewer products of interest. An ideal catalyst would operate with a high current density at low overpotential to selectively produce a desired product.

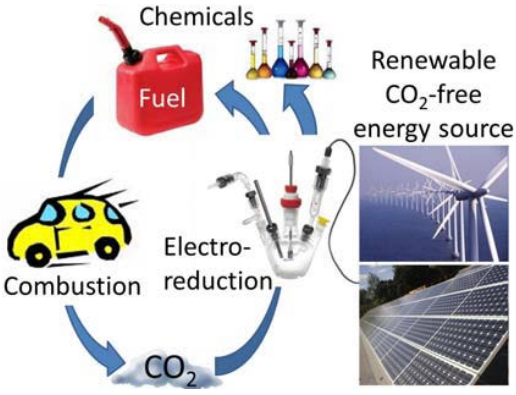

Figure 1: The goal of this research is to design electrocatalysts at the atomic scale to reduce CO_2 to fuels and industrially important chemicals. Coupling this reaction to renewable, CO_2-free energy, e.g. wind or solar, would enable a fuel cycle with net-neutral CO_2 emissions.

Approach

A theory-guided approach will be used to develop advanced catalysts for the electrochemical reduction of CO_2 and CO to fuels and chemicals. The Nørskov group has pioneered the theoretical description of the CO_2 and CO electro-reduction process [3]. The most promising catalyst surface structures identified by theory will be synthesized and investigated experimentally for catalytic activity, selectivity and stability. Jaramillo's group has developed state-of-the-art experimental methods for the CO_2RR, recently applying them to the study of polycrystalline copper electrodes [4]. Prior to that study, a total of 11 different CO_2RR products had been identified in the open literature on copper electrodes. In one consistent set of experiments, Jaramillo's group observed all 11 of those products, along with five new ones never reported previously. In addition to identifying those 16 products, Jaramillo's experimental methodology also allowed for quantitative tracking of the faradaic efficiency and the reaction rate of each product as a function of applied potential. This work provided the most complete information ever reported as to how copper catalyzes the CO_2RR. With this data set, the Jaramillo group was then able to construct plausible reaction networks, and provide novel mechanistic insights into the catalyst's activity and selectivity, as well as the molecular-scale phenomena occurring at the electrode-electrolyte interface (Figure 2), [4].

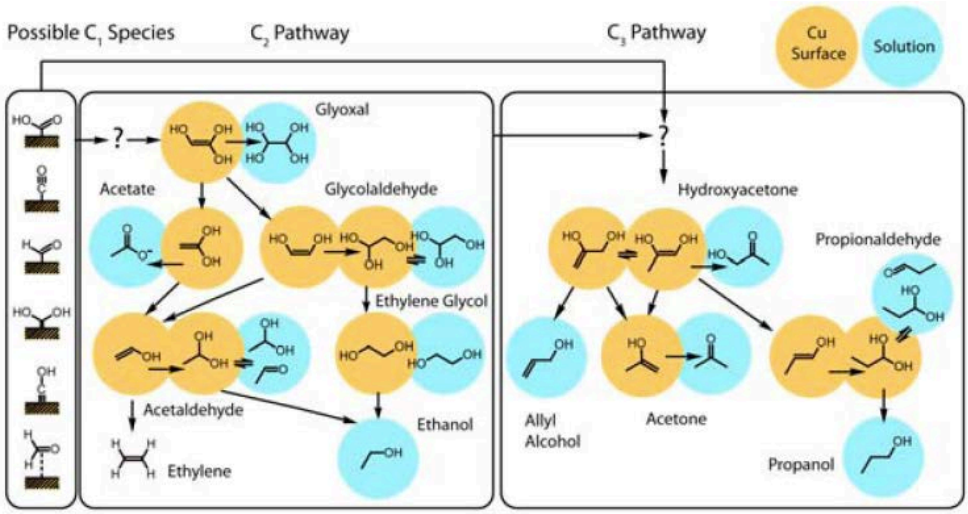

Figure 2: Proposed CO_2RR reaction network for a copper electrode, made possible by the high- sensitivity and quantitative nature of the experimental methodology in Jaramillo's laboratory.

The experimental component of this project will provide feedback to the underlying theory, allowing for improvements to the computational models that will help focus the theory towards the most pressing challenges as they are identified. Experiments in this project will also feature the use of sophisticated *ex-situ* and *in-situ* spectroscopic techniques to investigate the most promising catalyst materials. The aim is to gain critical, fundamental insight as to the physical and chemical nature of the catalyst, particularly as it executes the reaction under operating conditions. By combining theory and experiment in this manner, new catalysts will be discovered, providing new insights on how CO_2RR catalysts work and the physical-chemical factors that govern their performance.

References

[1] Vesborg, P. C. K.; Jaramillo, T. F. *RSC Advances* 2012, 2, (21), 7933-7947
[2] Hori, Y.; Kukuchi, K.; Suzuki, *S. Chem. Lett.* 1985, 1695.
[3] Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jonsson, H. *Journal of Physical Chemistry B* 2004, 108, (46), 17886-17892.
[4] Kuhl, K. P.; Cave, E. R.; Abram, D. N.; Jaramillo, T. F. *Energy & Environmental Science* 2012, 5, (5), 7050-7059.