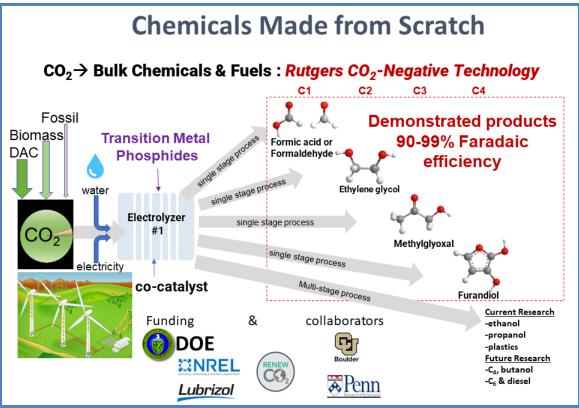
2023 W. Allan Powell Chemistry Seminar Series Friday, February 10, 2023

Your Future/Your Planet/Your Choice: The Truth About Biofuels, Neither Green Nor Economical vs. Carbon-Negative Chemicals & Fuels by Electro-synthesis from Carbon Dioxide

Charles Dismukes

Distinguished Professor Department of Chemistry & Chemical Biology Waksman Institute of Microbiology Rutgers University, 123 Bevier Rd, Piscataway, NJ USA dismukes@rutgers.edu

Abstract



The solar-to-biomass energy conversion efficiency of the three most widely used energy crops (sugarcane, corn and palm oil) is below 0.5%. Subsequent conversion to a biofuel (ethanol or biodiesel) produces an additional 2-fold loss or more in energy capture. Advanced biofuels represent a highly inefficient source of fuels and chemicals when compared based on their solar footprint (land use) and energy conversion efficiency. To mask this reality, biofuels have been promoted

as a renewable energy solution that can reduce greenhouse gas (GHG) emissions when replacing fossil fuels. Typically, coal-fired electricity plants are the inappropriate benchmark used for comparison. However, biofuels are major producers of GHG emissions per unit of energy produced, even though current yields meet only a fraction of the world demand. A consequence of this misrepresentation is that land cultivation of dedicated energy crops has risen dramatically worldwide by displacing natural ecosystems, food crops and pasturelands. By contrast, solar fuels produced from carbon dioxide and water by Artificial Photosynthetic (AP) technologies outperform biofuels by 3- to 5-fold in terms of energy conversion efficiency, they free-up an equivalent area of arable land, they are net CO2 consumers that reverse GHG emissions, can make fuels anywhere needed using highly distributed electrical power, and they respond rapidly to the intermittency of renewable electricity. Replacing biofuels with AP using CO2 sourced from waste from food crops and forestry wastes offers a transitional solution for CO2 capture and conversion to synthetic fuels and chemicals that leverages the advantages of natural and man-made approaches without the disadvantages of energy crops.

AP technologies for synthesis of industrial chemicals from CO2, water, and renewable electricity is an essential goal for chemical industries aiming to meet IPCC goals for greenhouse gas emissions. To accomplish this, electrocatalysts must be created that operate in ionic conducting media, at high current densities under ambient conditions (T, P) with product selectivity and low corrosion. The nickel phosphide family of six compounds (NixPy) incorporates the proven chemical principles of methanogenic/acetogenic biocatalysts. As electrocatalysts they operate at ambient temperature achieving turnover frequencies for endothermic reactions that would require T >1,000°C. Their functional sites are phosphino-dihydrides (*P-H(H)) and oxyanion binding sites (*Ni) possessing tunable chemical potentials that depend upon composition (x, y) and electrical potential (Vapplied) that determine the branching between *formic acid and *CO intermediates in the first step leading to different terminal products. Further tuning of selectivity to C1, C2, C3, C4, and polymeric products is achieved using either acid/base co-catalysts or atomic doping to control the desired reaction type: reduction/deoxygenation/dehydration/isomerization. Examples supporting the above claims will be highlighted and chemical mechanisms will be discussed.

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