JCAP Scientific Advances

The Joint Center for Artificial Photosynthesis (JCAP) was established by the U.S. Department of Energy in 2010 as the Fuels from Sunlight Energy Innovation Hub to advance the science needed to convert sunlight, water and carbon dioxide into a range of commercially useful fuels. Since its founding, JCAP has addressed numerous scientific and engineering challenges necessary to meet its goals, including efficient use of sunlight, water, and carbon dioxide, discovery of abundant and effective light absorbers and catalysts, a better understanding of how catalysts function within their environment, and development of integrated systems. This document summarizes progress in several areas; JCAP's publications [https://solarfuelshub.org/publications] provide more detailed information.

Improved performance and durability

JCAP's goals have included demonstration of solar fuels generation with a solar-to-chemical conversion efficiency that exceeds that of plants. This has required improvements in all materials used in solar fuels systems, as well as the systems themselves. The optimum photoabsorbers[1] will be stable under illumination in the aqueous electrolyte supporting coupled water oxidation and fuel forming reactions, absorb the solar spectrum efficiently, have band edges aligned with the potentials required for water oxidation and proton or CO_2 reduction, and produce a photovoltage sufficient to overcome any electrocatalytic and other overpotentials. While the main effort has been to satisfy these requirements using thin films, JCAP has also investigated designs of semiconductor nanostructure arrays that enable near-unity absorption of light,[2] an additional route to improved efficiency. To accelerate the process of discovery of new materials, JCAP has developed a high throughput pipeline that couples experiment and theory,[3] leading to exploration of complex compositions with the requisite physical and chemical attributes.

JCAP has also sought to understand factors that lead to instability in use, such as semiconductor corrosion,[4] which results from formation of material phases at the liquid-solid interface that are soluble at the operating potentials and pH environment, and catalyst dissolution.[5] One anti-corrosion strategy is stabilization through self-passivation, leading to identification of new photoactive materials such as n-$FeWO_4$.[6] Alternatively, high performance protection layers[7] can be deposited to mitigate corrosion while facilitating charge transport within the layer and at its interface with the electrolyte, as demonstrated with Ti oxide,[8] Co oxide,[9] and Sn oxide.[10]

Polyelectrolyte membranes are expected to be key components in solar fuels systems. They preserve efficiency by minimizing product crossover while conducting ions between the anode and cathode regions. There is a tradeoff between these two functions, and modeling[11] by JCAP has served to establish the associated device-driven specifications. Experiments[12] and simulations[13] have been used to characterize membrane permeation by typical CO_2 reduction products far from steady state, which is unlikely to be achieved in real systems due to daily and seasonal variability in solar intensity. New anion-conducting polymer designs, desirable for CO_2 reduction conditions, have been investigated to identify the correlation between composition and permeability,[14] and to confer polymer stability[15] during operation in electrolytes with elevated pH.

Understanding the role of catalyst environment in catalytic activity and selectivity

The surface structure of active sites and the surrounding chemical environment and electrochemical conditions comprise the major factors influencing the efficiency and selectivity of (photo)electrocatalysts for oxidation of water to form O_2 at an anode, and fuel formation at a cathode. JCAP has investigated combinations of materials, catalytic environments, electrolytes, and operating conditions that realize reduced overpotential (for efficiency) and improved selectivity for desired products while avoiding deactivation mechanisms. New catalysts have been developed for acidic electrolytes used in hydrogen generation systems, such as CoP[16] for hydrogen evolution and Mn-Sb-O[17] for oxygen evolution, and quinary lanthanide-Co-Fe-Ni oxide[18] catalysts for oxygen evolution in basic electrolytes. The nanostructure[19] of the quinary catalysts reduces overpotential[20] below those of the more widely used one- or two-metal catalysts such as Ni-Fe oxides. JCAP has evaluated metal electrodes for reduction of CO_2 using mechanistic theory and experiments, and has confirmed that copper and its alloys are the only materials that have sufficient activity to form fuel products by driving C-C coupling[21] efficiently. The surface morphology[22] of the catalyst plays a significant role in selectivity toward specific classes of products. JCAP has improved activity and selectivity by tandem electrocatalysis[23] schemes in which CO_2 is reduced to CO, and CO is further reduced to desired products. While efficient photoelectrochemical water splitting is most readily obtained with extreme acid or base electrolytes,[24] selective CO_2 reduction to liquid fuels by copper requires neutral to basic electrolytes.[25] JCAP has investigated how the concentration and identity of the cations[26] and anions[27] present in solution strongly influence the efficiency of CO_2 reduction. Water[28] also plays a role not only as a source of H, but also through its interactions with interfacial intermediates. Selectivity is also markedly affected by molecular additives[29] such as pyridiniums in the electrolyte, as well as polymeric overcoats[30] on copper surfaces. Because electrocatalysts change their structure when in contact with liquid and under an applied potential, JCAP has relied on *in situ* and *operando* measurements to characterize the actual catalytic environment. For example, JCAP has directly observed the dynamic evolution of Cu[31] under bias and in contact with electrolyte, which influences activity and selectivity.[32] JCAP has used these techniques to investigate the properties of interfacial double layers,[33] identify active sites in $NiFeO_x$,[34] and trace redox activity in IrO_x both with[35] and without[36] illumination.

Connecting photoexcitation and chemical reactions

Semiconductor photoabsorbers provide the electrons and holes required for artificial photosynthesis, and JCAP has performed studies that trace generation, relaxation and loss processes of charge carriers using transient absorption,[37] conversion efficiency[38] and photoemission[39] techniques. These studies provide information on how charge carrier generation is connected to photoabsorber composition and structure, particularly for metal oxides that may offer low cost alternatives to III-V semiconductors but typically suffer from low charge carrier mobility and photovoltage. The use of photoabsorbing cathodes to control selectivity for heterogeneous CO_2 reduction has been an important goal for JCAP. Because traditional photoelectrocatalytic materials such as Cu_2O are unstable, new materials have been sought using theory[40] as a guide. JCAP has investigated the use of photogenerated hot carriers,[41] plasmonic[42] and photonic[43] structures to couple light to chemical reactions and has found that this approach is a promising means to steer selectivity toward desired products.

Integrated systems design for high performance

Solar fuels systems function by integrating photoexcitation, chemical transformation and transport processes across broad length and time scales. A fundamental challenge is how to design system components so that the resulting combination of architecture and processes leads to optimum performance. A typical system will involve photoabsorbers, oxidation and reduction catalysts integrated with them, membrane separators, and water. JCAP has invested considerable effort in the design and fabrication of these components and test bed devices using them. Synthetic processes for integration of catalysts with photoabsorbers can be designed to optimize[44] interfacial structure and compositions. The challenge when both photoabsorber and catalyst are composed of multiple chemical elements is significant, and JCAP has developed high throughput techniques[45] to identify high-performing integrated systems. Selection of integrated components for full systems is guided by detailed multiphysics modeling,[24] which examines their performance characteristics within specified designs. JCAP has found that modeling is particularly important for CO_2 reduction systems due to performance constraints placed by internal transport[46] limitations and the variation of product distributions during a diurnal[47] cycle. JCAP has reported designs and demonstrations for solar-driven liquid electrolyte water splitting systems, progressively increasing solar-to-hydrogen efficiency performance by materials improvements from <1%[48] to 19.3%.[49] A sustainable technology[50] requires that a system be durable for years under the variable operational conditions. While this goal remains a challenge, JCAP has reported strategies for stabilizing systems while ensuring >10% solar-to-hydrogen efficiency with full product separation (for safety). These include use of TiO_2 protection layers[51] and hybrid composite coatings[52] to inhibit corrosion in electrolytes at extreme pH. High efficiency and stability has also been demonstrated in a vapor-fed photoelectrochemical system[53] using pure water, which minimizes corrosive conditions. The high overpotentials required for C-C coupling during photoelectrochemical CO_2 reduction pose additional challenges. JCAP has demonstrated a photocathode[54] design useful for liquid electrolyte systems, identified gas diffusion electrode[55] architectures as being particularly useful for CO_2 reduction, and exploited potential multistep strategies that reduce CO,[56] which can be formed as a reaction intermediate. These efforts establish technology-driven performance criteria for individual materials and integrated systems that guide materials discovery and development efforts.

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