Storing sunlight at low temperatures?

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Artificial leaves that convert sunlight to fuels could provide a sustainable energy future. But several challenges must be overcome to improve their economic viability. Publishing in *Energy & Environmental Science*, Kölbach, Rehfeld, and May describe the potential of decentralized hydrogen production using thermally integrated architectures that operate under sub-freezing temperatures.

Since Giacomo Ciamician's prediction of a solar-fueled future published in 1912,[1] scientists have been inspired by the biochemical process of photosynthesis to develop artificial leaves that use sunlight to create fuels and other value-added chemical products. Such solar-to-fuel devices could enable carbon-free or carbon-neutral pathways to powering the planet.[2] Accordingly, their pursuit has been described as a scientific and moral challenge of our time.[3] Recent research from Kölbach, Rehfeld, and May brings this vision of a solar-fueled future a step closer to fruition.[4] Their work, published in *Energy & Environmental Science*, titled "Efficiency gains for thermally coupled solar hydrogen production in extreme cold", describes benefits that become possible with higher levels of artificial leaf device integration.

The construction of artificial leaves has been pursued using a continuum of design concepts.[5] As depicted in Figure 1, these range from more decoupled approaches such as photovoltaic-powered electrolysis (PV-electrolysis), to more integrated designs such as those used in photoelectrochemistry (PEC). In PV-electrolysis, photovoltaic components are interconnected to power physically separated electrolyzer units. The electrolyzers contain catalysts—chemical sites providing low-energy pathways for driving energetically uphill reactions such as the splitting of water into oxygen and hydrogen. These chemical products can be used as fuels or stored for later use, including chemical upgrading. The other approach of PEC offers the same advantages regarding its chemical products, but here the light-harvesting and electrocatalytic components are co-located and/or assembled into a single architecture.

Both design strategies are inspired by the biological process of photosynthesis, where plants and other organisms store the sun's energy in the form of chemical bonds that constitute the foods we eat and ultimately, on longer geological timescales, the carbon-based fossil fuels our modern societies rely on. However, key distinctions between PV-electrolysis and PEC include their technological readiness level (TRL), raw material requirements, cost, and potential for scalability. PV-electrolysis is a more mature technology that benefits from its modularity, enabling the individual components to be optimized for their integrated operation. PEC devices, on the other hand, promise simplification of device architecture and thereby lower costs, but they are technologically less mature and thus remain active areas of research[6] with correspondingly more limited market penetration.

The work from Kölbach, Rehfeld, and May now provides evidence and experimental credence for advantages that can be realized using higher levels of artificial leaf device integration.[4] The authors leverage a fundamental difference in favored operating temperatures of traditional light-absorbing semiconductors—which achieve higher efficiencies at cooler temperatures—versus catalytic materials—which favor operating hot. By thermally coupling semiconductor light-harvesting materials with electrocatalytic components, the authors show that an integrated design can use waste heat from the light absorbers to both reduce the internal device electrical resistance and decrease the energetic requirements of catalysis (Figure 2). In turn, the cooling of the absorbers boosts their efficiency.

Although the authors describe applications limited to relatively cold climates,[4] their research could enable pathways to developing these niche applications into technologies for sustainable hydrogen production[7] with global-scale market penetration. As an example, technological maturation of photovoltaics was fostered by applications initially slotted to space exploration. Further, the upfront development of semiconductor transistors—now a basic building block of modern electronics—was confronted with skepticism. "Only 20% of them worked. They were hard to manufacture. They required the design of new kinds of circuits. Even if they could eventually, theoretically, replace the vacuum tube, the tube worked well enough. How could they be worth the trouble?"[8]

In comparing the efficiencies achieved by biological photosynthetic organisms versus artificial leaves, the bioinspired constructs already fare comparatively

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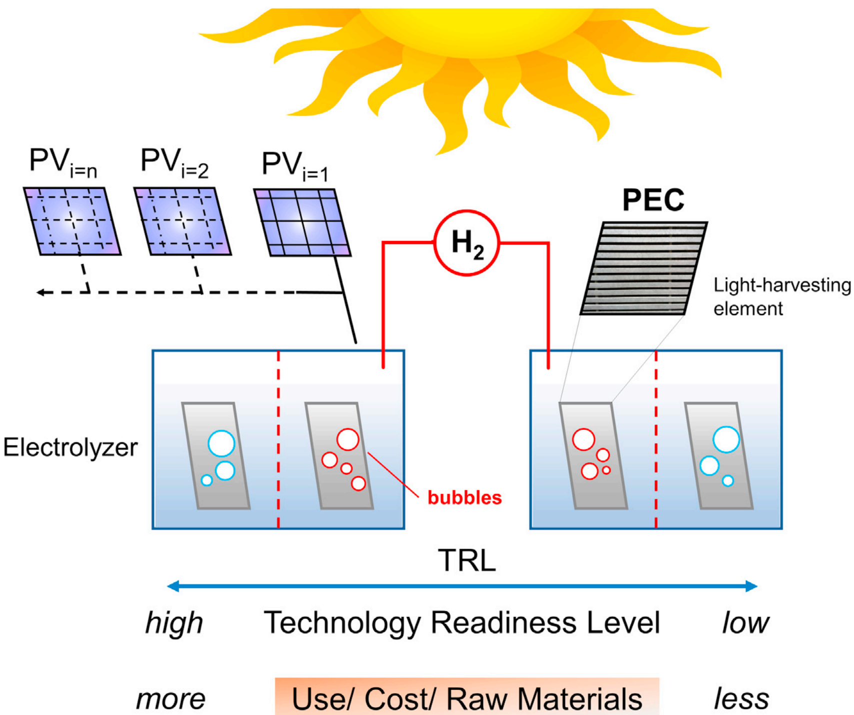

Figure 1. Schematic comparing photovoltaic-powered electrolysis (PV-electrolysis) (left) and photoelectrochemical (PEC) (right) device concepts, including tradeoffs in their current use, projected costs, required amount of raw materials, and current technology readiness level (TRL)

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well.[9] The efficiency of the initial light capture and charge separation steps in natural photosynthesis can reach unity under relatively low light fluxes; however, losses related to metabolism and the use of intermediate energy carriers reduce their overall solar-to-fuel efficiencies to less than a few percent. Artificial photosynthetic assemblies that operate with solar-to-hydrogen efficiencies >10% are already commercially available.[9] Of course, using a single figure of merit such as efficiency can be deceptive, and other factors such as cost and stability should be considered. For example, the overall solar-to-fuel efficiencies of biological photosynthetic organisms are relatively low, but they assemble a wide range of complex chemicals and are composed of Earth-abundant materials. They also have the ability to repair themselves, reproduce, and evolve.

Outstanding challenges in the field of solar fuels and artificial photosynthesis include not only achieving higher efficiencies, but also fabricating materials that use relatively low-cost components that are robust and thus scalable. In the context of hydrogen production, how to store and transport this product for applications in global markets also remains an outstanding issue. Further challenges include using the principles of green catalysis to re-engineer or entirely recreate the processes and technologies required to produce the range of chemicals our modern societies rely on. This includes manufacturing reduced forms of carbon dioxide and dinitrogen as well as creating imaginative ways of rebalancing the planet's phosphorus cycle. Carbon dioxide is a major greenhouse gas contributing to global climate change. Its photo-driven reduction could contribute to a cleaner energy future; however, there are concerns regarding the viability of using carbon dioxide to fabricate fuels. These include the scale of the related energy-intensive processes and the energy return on energy investment.[10] The photo-driven reduction of dinitrogen to ammonia is another challenge for photochemistry. Unlike the reduction of water to hydrogen and carbon dioxide to reduced forms of carbon, the reduction of nitrogen to ammonia is energetically downhill. In spite of this, the century-old and energy-intensive Haber–Bosch process for converting nitrogen and hydrogen to ammonia remains the sole industrially relevant method for generating the nitrogen fertilizers used for approximately half of all global food production. The scale of this industrial process is sobering. Nearly 80% of the nitrogen contained in all human tissue originates from the Haber–Bosch process.[11]

Indeed, human activities have pushed the biological process of photosynthesis to its limits, affecting multiple Earth systems that are central to balancing Earth's resource budget.[12] Rather than exploiting the products of natural photosynthesis, human ingenuity and our knowledge of photosynthesis could be leveraged to pioneer new technologies with properties and capabilities rivalling those of their natural counterparts. Advances such as those described in the article of Kölbach, Rehfeld, and May showcase such possibilities. But energy issues are complex, tightly coupled to human behavior, and will likely require social as well as political obstacles to be overcome.

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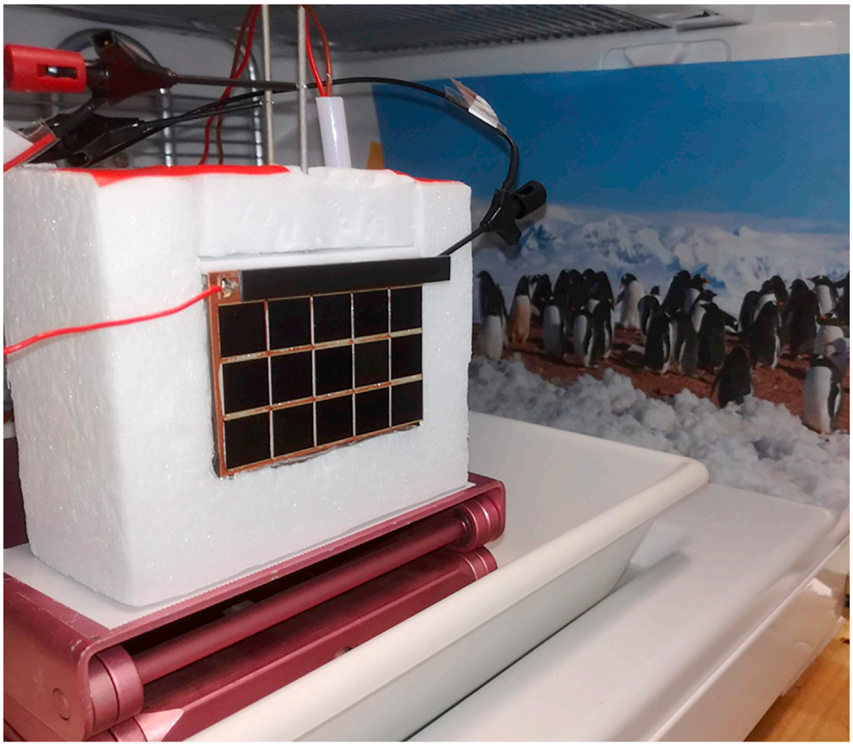

Figure 2. An image of the thermally integrated solar-water-splitting device studied by Kölbach, Rehfeld, and May

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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