An Integrated, Systems Approach to the Development of Solar Fuel Generators

by Nathan S. Lewis

Two major technological challenges in the development of a sustainable, clean energy system are providing massive grid-scale energy storage and an ample supply of carbon-neutral, high-energy-density, transportation fuels. The development and deployment of massive, grid-scale energy storage is imperative for reliably and robustly compensating for the intermittency involved with the utilization of very large amounts of wind energy and solar energy.[1] Another challenge is that ~ 40% of current global transportation fuel is consumed in uses for which electrification is technically difficult, if not impossible, such as in heavy-duty trucks, ships, and aircraft.[2] Exhaustive use of advanced biofuels might possibly supply adequate carbon-neutral transportation fuel for these uses, but could not then also fulfill the requirement for long term, massive, grid-scale energy storage.[3] Chemical fuels are desirable for energy storage because fuels are the most energy-dense storage medium known to man (other than the atomic nucleus), and could simultaneously provide a means to baseload at scale intermittent renewable energy resources while also fulfilling gaps in the need for high energy-density, carbon neutral, sustainable, transportation fuels.[4] Hence a clear rationale exists to develop technology options that involve the conversion of sunlight, by far the largest energy source, directly into chemical fuels.

One approach to address both of these technology development imperatives involves the development of artificial photosynthesis. In artificial photosynthesis, sunlight is directly converted, without the use of (or the limitations of) living systems, into a useful chemical fuel.[5] Artificial photosynthesis has been pursued in the laboratory for over 40 years, since the observation by Fujishima and Honda that exposure of TiO_2 to sunlight effects water splitting to produce, with high quantum yields, H_2 and O_2.[6] However, to date, no single light absorber for artificial photosynthesis has been shown to combine simultaneously three desired technological attributes: efficiency, affordability, and robustness.[7] A manufacturable artificial photosynthesis system also involves much more than a single photoelectrode, necessitating the incorporation of suitable catalysts, materials for the separation of the products, mitigation of undesirable effects of bubbles and flows, methods to manufacture the system at scale, and approaches to encapsulate the materials while maintaining facile reactant access and product egress. The requirements that are imposed on the components therefore depend intimately on the design of the whole system. Hence, optimal progress toward a viable solar fuels technology mandates a holistic, systems approach, to identify and then solve the research and development needs that historically have served as barriers to the development of a scalably-manufacturable solar fuels generator.

Natural photosynthesis provides a complex, but elegant, blueprint for the production of fuels from sunlight. With only water, carbon dioxide, and sunlight as the inputs, solar energy is stored in the form of chemical bonds as the output of photosynthesis. However, natural photosynthesis has significant performance limitations at the systems level, such as saturation at approximately one-tenth the peak intensity of sunlight; relatively modest overall energy conversion efficiencies on an annually averaged basis (1% or less); the need to spend significant amounts of energy internally to regenerate the unstable enzymes and to resynthesize the highly exquisitely ordered and arranged molecular machinery of photosynthesis; and in general the production of a fuel that is not directly compatible with widespread use in existing energy systems.[8] Production of fuels directly from sunlight is thus inspired by natural photosynthesis, but has the mandate to provide far superior performance than photosynthesis. In this respect, "performance" is measured by the net annually averaged energy conversion efficiency to produce a useful chemical fuel in a scalable, cost-effective fashion. A fully artificial photosynthetic system would also not require arable land, potable water, or involve tradeoffs of land to be used either for food or for fuel production.

It is clearly possible to construct a fuel-producing, man-made, solar energy-conversion system that outperforms natural photosynthesis on an efficiency basis. For example, solar panels can be over 30% efficient in conversion of sunlight into electricity.[9] In turn, electrolyzers can take electrical energy and produce H_2 and O_2 from water at over 70% energy efficiency.[10] Hence, in combination, the sunlight to fuel (in this case solar-to-hydrogen, STH) energy-conversion efficiencies of a modular photovoltaic/electrolyzer combination system can be over 10 times greater than that of the fastest growing plants (on a yearly average). A goal of research in artificial photosynthesis is however not only to demonstrate high efficiency, but to develop a technology that is the basis for a fully integrated solar fuels generator system that can simultaneously combine the three desired attributes of cost-effective scalability, robustness, and efficiency.

A fully integrated artificial photosynthesis system is a complex assembly that will need to bridge many length scales, likely over as many as seven orders of magnitude (Fig. 1). The requirements, outcomes, and success of the R&D at each scale length are intimately dependent on the requirements, success, and outcomes of the R&D needed to construct such a system at many other scale lengths. For instance, the requirements on the materials used for light capture on the nanoscale depend significantly on the form factor and architecture of the system developed as a prototype on the cm-to-m length scale. Similarly, success on the μm length scale for the production of fuels from sunlight will generally produce bubbles and flows of product that would, if not controlled or mitigated, degrade the performance of the system on the m length scale. Rapid progress therefore is facilitated by vertically integrated R&D efforts that simultaneously address a multitude of critical bottlenecks at a multitude of length scales, in a parallel, spiral development type of structure.

Technology Bottlenecks in the Development of an Integrated Solar Fuels Generator System

System components.—Figure 2 identifies some of the key bottlenecks that currently prevent the demonstration and construction of a scalably-manufacturable solar fuels generator system. Clearly, suitable materials are needed for the capture and conversion of sunlight. In photovoltaics, current can be traded for voltage, so materials with a relatively wide range of band gaps can be used to produce mutually similar net electrical power as the system output. However, the production of fuels, such as the prototypical example of splitting water into H_2 and O_2, requires a minimum voltage of 1.23 V, below which, according to the first law of thermodynamics, no substantive net products will be produced.[11] Hence, materials that are well-suited for light capture for solar fuels production are not fully contained in the set of materials that are used for production of photovoltaics.

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The presence of kinetic and concentration overpotential losses in electrochemical systems,[11] as well as the difference between the voltage of operation at maximum power production relative to the open-circuit voltage produced by a solar light absorber, imply that a single threshold system probably requires a band gap of at least 2.0 eV, and more likely at least 2.2 eV.[12,13] However, the solar spectrum contains relatively few photons that are capable of providing such high excitation energies;[14a] therefore the ultimate energy conversion efficiency of the resulting photosystem is limited to <10%. In contrast, the use of two light absorbers that are connected electrically in series, each of which contributes a portion of the needed photovoltage for the fuel-production process, can provide ultimate solar-to-fuel energy conversion efficiencies of >25% (Fig. 3).[14b] This type of artificial photosynthesis design therefore closely resembles the "Z-scheme" employed in natural photosynthesis.[15]

Once electrons (actually electron-hole pairs) with the required energetics are produced, catalysts are generally needed to facilitate the efficient production of chemical fuels. The need for catalysis can be readily understood at the fundamental level because the sun is not a laser! Hence solar photons strike a device one at a time, but two or more electrons are needed at once to make and/or break chemical bonds (2 electrons to reduce water to H_2, 4 electrons to oxidize two molecules of H_2O to produce one molecule of O_2, 6 electrons to reduce CO_2 to CH_3OH, etc.). The required electrocatalysts must be highly active, stable, and, for global scalability, must be either comprised of earth-abundant elements or must minimally utilize scarce metals such as Ru or Ir. Unfortunately, the most active catalysts for water splitting (in acidic environments) are Pt and IrO_2,[7] so a goal for the global solar fuels research and development community is to discover, develop, and exploit suitable systems and architectures that can allow for the replacement of large quantities of these scarce transition metals with more abundant metals, such as Mo, W, Co, Ni, Fe, or Mn.

A suitable half-cell electrocatalyst alone does not of course suffice to provide an adequate blueprint for the construction of a fully operational solar fuels generator system. The oxidative and reductive electrocatalysts need to work under mutually compatible conditions of pH, temperature, etc. The electrocatalysts also need to be interfaced with the light capture components, while retaining as an assembly the function of all of the individual pieces. The system must also be capable of operating safely with minimal, if any, co-evolution of H_2 and O_2 to produce an explosive gas mixture. Similarly if CO_2 is reduced to form methanol, for example, the methanol must not diffuse to the oxidative region of the system, or it will be oxidized back to CO_2 and the overall system efficiency will be unacceptably degraded.

Hence, a membrane, or some type of physical and chemical separation system, is needed to prevent deleterious product back-diffusion or convention. But production of O_2 from water will produce protons, whereas the reductive formation of a fuel
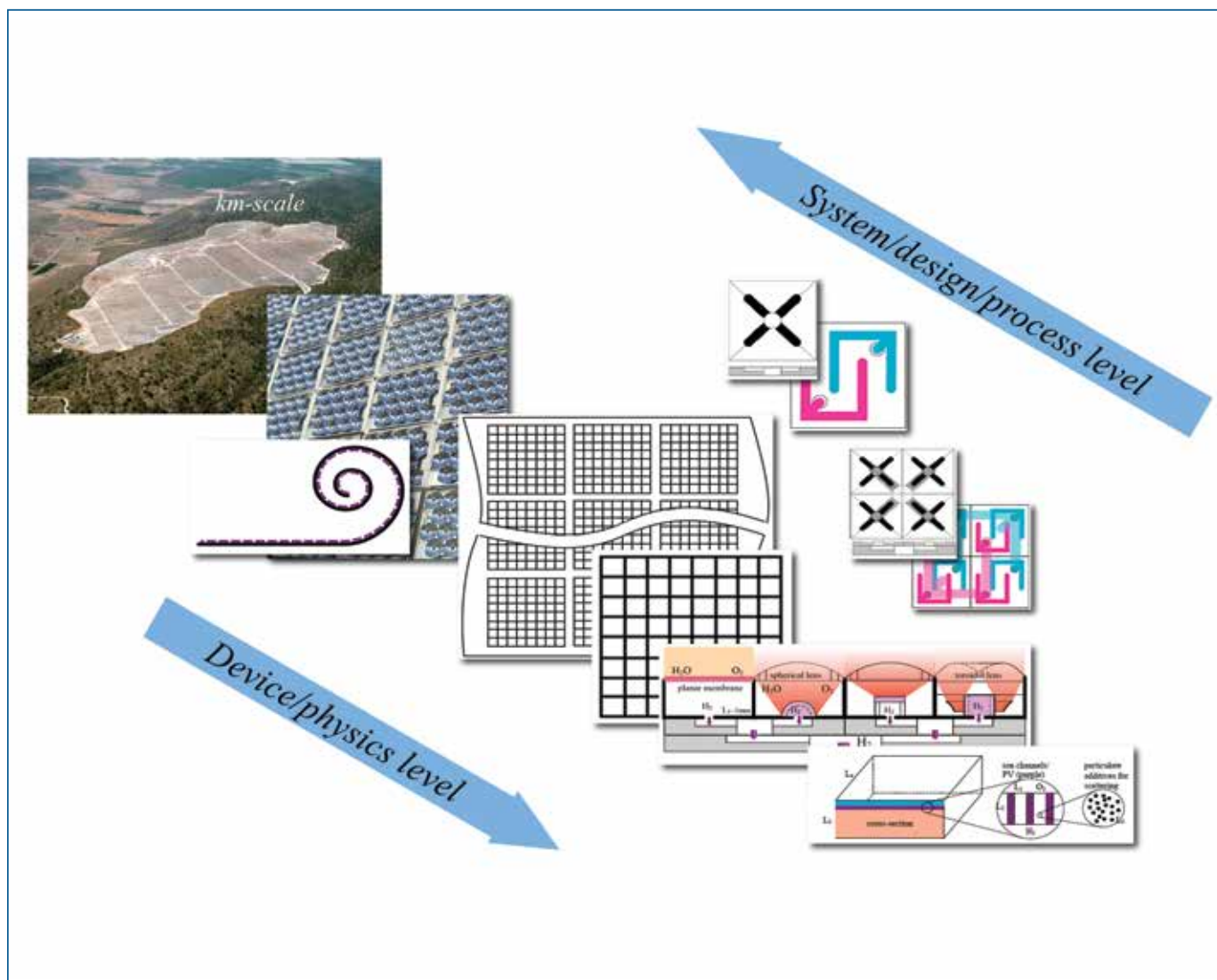

Fig. 1. *Development scale of an artificial photosynthesis system.*
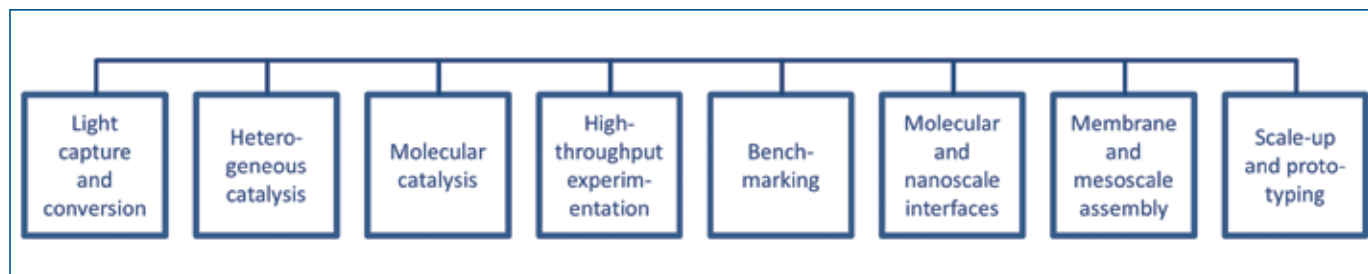
Fig. 2. *Some key R&D bottlenecks in development of a solar fuels generator system.*

will consume protons. The system must therefore allow a facile, low-resistance, path for ion (generally proton or hydroxide) conduction to neutralize the pH gradient, else the net reaction to form products will cease to occur. For this reason, a key R&D opportunity in the development of a solar fuels generator system is the development of suitable membranes or alternative physical/chemical/mechanical product separation schemes for enabling a scalable, manufacturable solar fuels generator.

Functional integration of components.— The best catalyst is of course not sufficient if, when combined with the best light absorber, the catalyst poisons the light absorber and in turn the light absorber poisons the catalyst. Hence another goal for the global solar fuels R&D effort is to develop "interfaces" or "integrated systems," which address strategies to link and interconnect the individual components of a system in a robust fashion with minimal loss of

performance in the process. A central focus of such efforts will involve understanding the inefficient charge transport between light absorbers and catalysts and, in particular, between the sites of water oxidation and fuel-generating half-reactions. Typically, a large fraction of the photogenerated electrons or holes are diverted from productive paths by back or side reactions, or are trapped at defect sites resulting in low photochemical quantum yields.

A critical challenge is achieving acceptable charge-transport efficiency at every stage of the catalytic cycle, which reflects the inherent difficulty of reconciling one-photon, single-charge generation with multi-electron catalysis. In addition, interfacial reactions during the deposition of metal catalysts on semiconducting light absorbers generally produce alloys or new compounds that introduce surface recombination sites in the light absorber and/or that reduce the catalytic activity of the metal electrocatalyst particles

in the half-cell reaction of interest. These effects can be mitigated, or in fact exploited beneficially, through the use of optically transparent metal films and/or through nanoscale control over the space-charge region of laterally inhomogeneous metal/liquid/semiconductor interfaces. Hence, R&D efforts devoted to understanding, and controlling, the interfacial chemistry of electrocatalysts integrated onto light absorbers is clearly an important component of a systems approach to development of a solar fuels generator system.

Benchmarking.—Another important component of a global solar fuels R&D effort is the development and implementation of standardized measurement methods and techniques for assessing the activity of electrocatalysts and photocatalysts for solar fuels production. To date, a variety of methods and procedures have been used to assess the (photo)electrochemical behavior of solar fuels generators, half cells, and catalysts. For example, the activities of heterogeneous electrocatalysts for water splitting are reported in their own, individual conditions of solvent, electrolyte solutions, and pH.[7] Additionally, samples of catalysts are generally deposited, using various techniques, onto mutually different substrates, and the resulting surface topographies and morphologies differ substantially between research groups. Even the definition of catalytic activity varies substantially, with some workers quoting the exchange current density and others quoting the overpotential needed to reach a given current density. The quoted quantities often do not allow for systematic comparisons across investigators or from catalyst to catalyst, due for example to differences in quoting the geometrical, BET active, or electrochemically active surface areas of the system being measured.

A very similar situation is present for photoelectrochemical systems and devices. Various investigators quote solar energy-conversion efficiencies using light sources that have mutually different spectral dependences, such as tungsten-halogen lamps, high-pressure Xe arc lamps, lasers, Hg lamps with or without filters that simulate Air Mass 1.0 or 1.5 conditions etc. The efficiency assessment is either
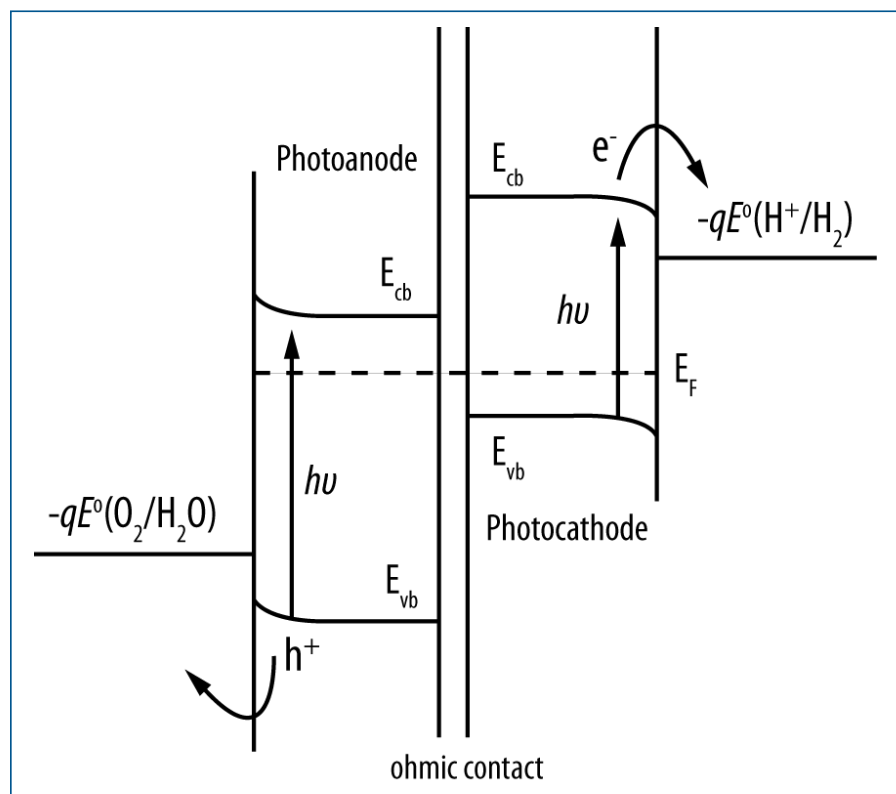
Fig. 3. *Energy diagrams for a tandem cell configuration with n-type and p-type photoelectrodes electrically connected in series.*

made by evaluation of the photocurrent-voltage characteristics of the system or by measurement of the production of fuels.[7] In addition, various methods have been used to calculate the efficiency of solar fuels production even from nominally the same type of system output data.[16]

A benchmarking effort should therefore involve the development and implementation of uniform standardized methods and protocols for characterizing the activities of catalysts for the oxygen evolution, hydrogen evolution, and CO_2 reduction reactions. One goal is the development of an internationally accepted facility that provides cross-comparable measurements on catalysts, half-cell systems and on devices, assessing their catalytic activity, solar conversion efficiency, and stability.

Figure 4 shows an example of catalyst evaluation in a multi-parameter representation. The abscissa displays the measured overpotential for the hydrogen-evolution reaction obtained upon immersion of the sample. These measurements have been performed in acidic, neutral, and alkaline aqueous solutions. The ordinate displays the overpotential measured after the catalyst has passed 10 mA cm^{-2} of current density for a period of 2 h. The color code displays the surface roughness factor that was determined by use of electrochemical impedance measurements.

In acidic solution, a NiMo alloy appears to have an overpotential that is comparable to that of Pt. Both catalysts exhibit considerable stability because the overpotential does not change significantly after 2 h of operation. In contrast, the overpotential for MoS_2 increases upon operation, as indicated by the location of the MoS_2 data point above the dashed line for acidic and neutral solution. The color code shows that the Ni-Mo electrocatalyst also has a substantially

larger surface area, as expressed by the measured roughness factor, when an activity is observed that is comparable to that of Pt. Consequently, the plot concisely reveals that the catalytic activity per surface area of Ni-Mo is considerably smaller than that of platinum. Population of such a plot by the global solar fuels community would greatly facilitate inter-comparison between the various global solar fuels R&D efforts.

Accelerated discovery.—Another important avenue for solar fuels R&D would address the need to dramatically accelerate the process of discovery of new light absorbers, photocatalysts, and electrocatalysts. Traditionally, several years of time, and several person-years of effort, are required to synthesize, purify, characterize, and then optimize an individual light absorber or electrocatalyst. Although such directed research activities must still proceed with vigor and on a global scale, these activities can beneficially be complemented by a highly parallelized, extremely rapid methodology that uses high-throughput experimentation methods.

A typical combinatorial approach involves the design of libraries that produce high information density in the discovery process.[17-19] The approach also includes a vectorial search component in the sense that families and compositional fields of lead components are specifically examined and selected. The combinatorial approach mandates rapid screening methods of the most relevant material properties at a speed that equals the rate of compound synthesis. An additional area of concern involves the differences between the (spatial) library density and the synthesis speed, given that the demands differ depending on the application.

For photoelectrochemical applications, combinatorial ink jet printing and sputtering have already been used to generate some modestly sized libraries of compounds,[20-22] in rather small daily volume. It is possible

however to systematically prepare very large libraries of compounds, in a standardized, reference-able fashion, using ink jet printing, sputtering, and electrodeposition methods. First-generation ink jet printing, using drop-on-demand technology, has allowed the synthesis of $10^2 - 10^3$ compounds per hour on FTO-coated glass. Reproducibility, mixing (sample compositional homogeneity) and thickness can be addressed by the replacement of layer-by-layer printing with a bitmap process in which interlaid patterns are created, and by surface pretreatments that reduce the liquid surface tension and surface hydration. For example, a library of 1844 samples can be produced within a few minutes at high resolution and low print velocity (Fig. 5). Such methods allow the synthesis of ~ 75,000 samples per hour with a single machine, therefore enabling a synthesis output of over one million samples per day assuming continuous operation of such an instrument.

High-throughput experimentation also needs fast and reliable screening methods to comprise a full research pipeline system. For light absorbers, a suitable initial screen would involve the determination of the energy gap and of its nature with respect to direct versus indirect transitions. The availability of several earth-abundant materials that can be used as photocathodes, such as Si and MX_2 (M=W, Mo; X=S, Se),[23,24] reduces the materials search predominantly to photoanodes that have band gaps between 1.6 eV and 1.9 eV.[14] Visual inspection of the prepared library plates allows exclusion of materials that are either transparent or opaque. For determination of the optical properties of the remaining samples, rapid diffuse reflection spectroscopy, by use of an integrating sphere, has been developed (Fig. 6). Further screening consists of electrochemical (electrocatalysts) and photoelectrochemical (light absorbers) analyses. Stability under operating conditions can then be assessed
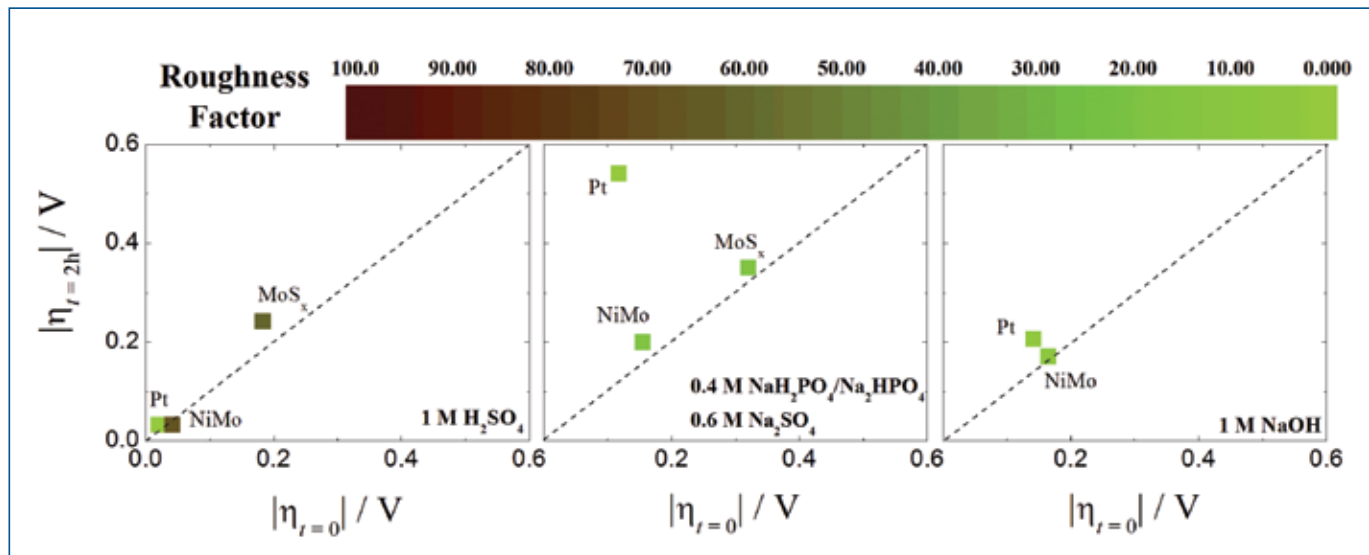

FIG. 4. *Benchmarking of electrocatalysts with regard to activity and stability.*

in aqueous solutions and for different pH conditions, along with determination of the composition and structure of entire collections of interesting compounds. The resulting databases should optimally be made available for use by the global research community, and also should be used to provide feedback to direct subsequent more refined high-throughput materials searches.

Understanding emergent phenomena on the mesoscale.—Even if suitable light absorbers, catalysts, and integrated systems are developed, important phenomena also exist on the mesoscale, *i.e.*, on the length scale of 100 nm-100 μm. A photovoltaic assembly that is constructed from a single semiconducting nanoscale object is of great academic interest, but a practical

solar fuels generator system will involve the preferential alignment of such objects over large areas, with the nanostructures pointing predominantly towards the sun, like blades of grass on a manicured lawn. Similarly, the optical, chemical, transport, and mechanical properties of an assembly

Fig. 5. *High-throughput plate with a materials library consisting of quaternary metal oxides of Ni, Co, Fe, and TiO_x. Synthesis conditions: the samples were aged at 100 °C, and then calcined at 350 °C for 6-8 h in air.*
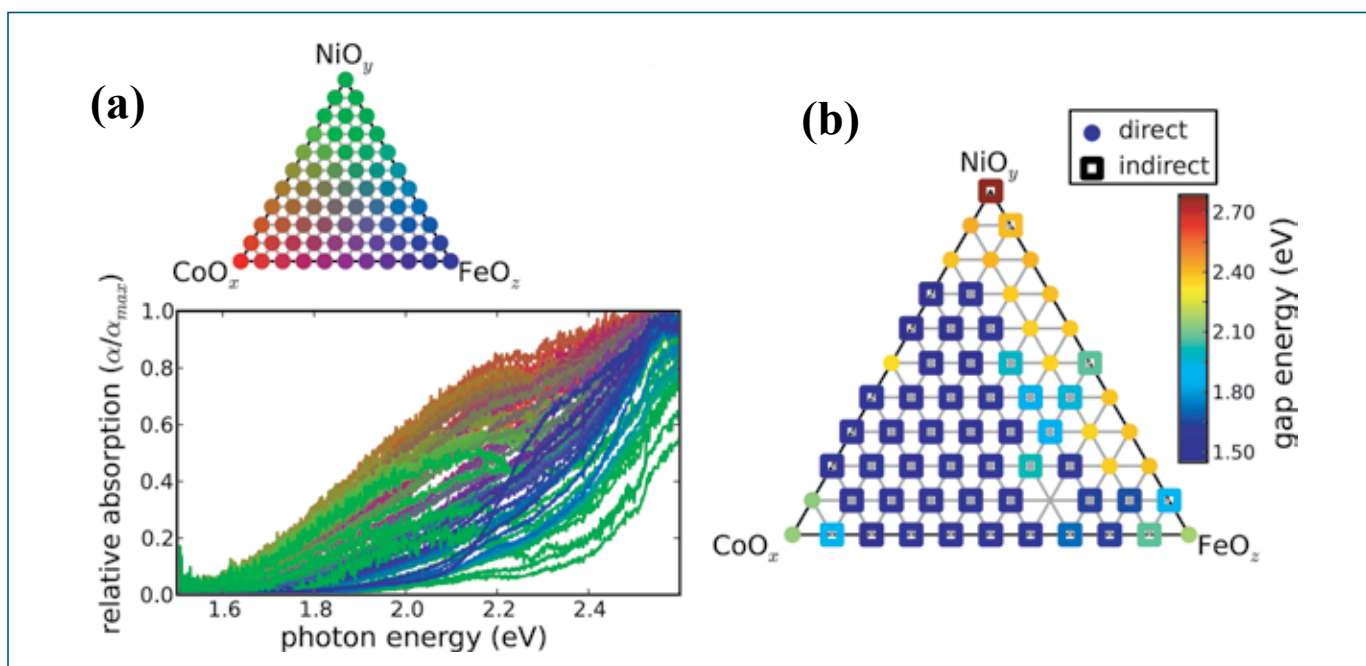
Fig. 6. *Screening of optical properties of an example materials composition field to determine suitable light absorbers: (a) relative absorption vs. photon energy, determined from evaluation of the diffuse reflection spectroscopy data; and (b) assignment of energy gaps and direct vs. indirect nature of the absorption edge.*

of nanostructured objects are not generally predictable from the properties of a single object by itself. Hence efforts are required to orient nanoscale objects of interest over large areas using self-assembly and scalably-manufacturable methods, as well as to understand the optical, electrical, electrochemical, chemical, mechanical, and physical properties of macroscopic assemblies of systems of hard materials embedded into polymeric, soft materials.

Membranes or other physical types of barriers are needed to separate the products while allowing for neutralization of the pH gradient that will be present otherwise as a result of the vectorial charge transport that is involved in the production of a reduced species (*e.g.*, H_2 or CH_3OH, etc.) spatially separate from the production of an oxidized species (*e.g.*, O_2). Some membranes are available for separation of products with acceptable ionic conductivity under acidic or alkaline conditions, but few, if any, membranes are available that can function at neutral or near-neutral pH conditions.[25-28] Similarly, few membranes have acceptable proton conductivities but low permeabilities to methanol and to other reduced carbon species from CO_2.[29] Hence R&D efforts at the mesoscale are needed to develop new types of membranes, with the needed properties, to support the functionality required for a solar fuels generator system.

From components to constructs to devices to prototypes.—At still larger scale lengths, the reactor design, reaction inputs and outputs, flow paths, assembly schemes, system integration issues, and physical layout of the light absorbers relative to each other, relative to the incident light path, etc. need to be specified. In turn, the arrangement of the components in the prototype affects the performance of the prototype as well as the requirements for the materials and

components that will be needed to provide optimal stability and efficiency for the prototype itself. Hence, R&D in solar fuels generator systems also requires a concurrent prototyping effort, to design, debug, model, construct, and evaluate the performance of a wide variety of physical embodiments of solar fuels generators, optimally even before the final components themselves are specified in detail.

Some of the critical system design criteria include: (1.) separation of the product gases, to produce minimal recombination; (2.) efficient neutralization of the pH gradient that will be produced by a spatial separation between the locations of water oxidation and water reduction; (3.) a low gas crossover rate, for safety purposes, to avoid having a gas mixture above 4% H_2 in air (the flammability limit) and surely to avoid having a gas mixture above 17% H_2 in air (the lower explosive limit); and (4.) the ability to hold back pressure differentials, to avoid gas and liquid flow in the system that will result from a pressure differential between different regions of the system (to collect the gas or gases obviously requires a pressure gradient, but the 2:1 H_2:O_2 stoichiometry of water electrolysis will produce, if not actively monitored and controlled, a significant pressure differential between the H_2- and O_2-evolving and collecting parts of the system).

These design criteria are common to both solar-driven electrolyzers as well as to conventional, electrical-driven electrolysis systems. However, in the absence of optics used to achieve solar concentration, the solar fuels generators will operate only at a projected area current density of 10-20 mA cm^{-2}, whereas to minimize the balance of systems and the area of the membrane-electrode assemblies, present electrically driven electrolysis systems operate at projected area current densities of ~ 1 A cm^{-2}. This difference potentially changes

the acceptable, or even optimal system geometric parameters and system design that would be needed to achieve acceptable operational performance.

A prototyping project could beneficially involve the use of electrochemical engineering design tools to evaluate the limitations and optimal operating conditions for several possible physical designs of an integrated solar fuels generator system. Each design (Fig. 7) should be evaluated with respect to the series resistance, the ability to hold back pressure differentials, gas crossover fluxes, and the fraction of the incident optical plane that is occupied by photoactive material that can absorb the incident sunlight. Resistance drops could be evaluated by use of a Poisson's equation solver in Comsol Multiphysics. Comsol, as well as analytical modeling where possible, could be used to evaluate the gas crossover fluxes driven by either diffusion or convection for the different geometries and physical parameters of the different designs.

The modeling effort would aid in the establishment of quantitative metrics for success for the various components based on their performance at the R&D level. For instance, one prototype may only possibly require an improvement in the light absorber band gap by 0.2 eV and then it is "done;" another prototype might have adequate light capture but require a H_2 evolution catalyst that is a factor of 15 better than the current state-of-the-art; yet another prototype may have adequate catalysts but the catalysts operate at mutually different pH values or at a pH value where no suitable membranes have yet been developed. In this way, both the modeling and reduction to practice of the various prototypes of solar fuels generators is critical towards establishing rigid performance metrics and for insuring that the R&D program solves problems that are in fact real problems and does not solve problems that are not problems.
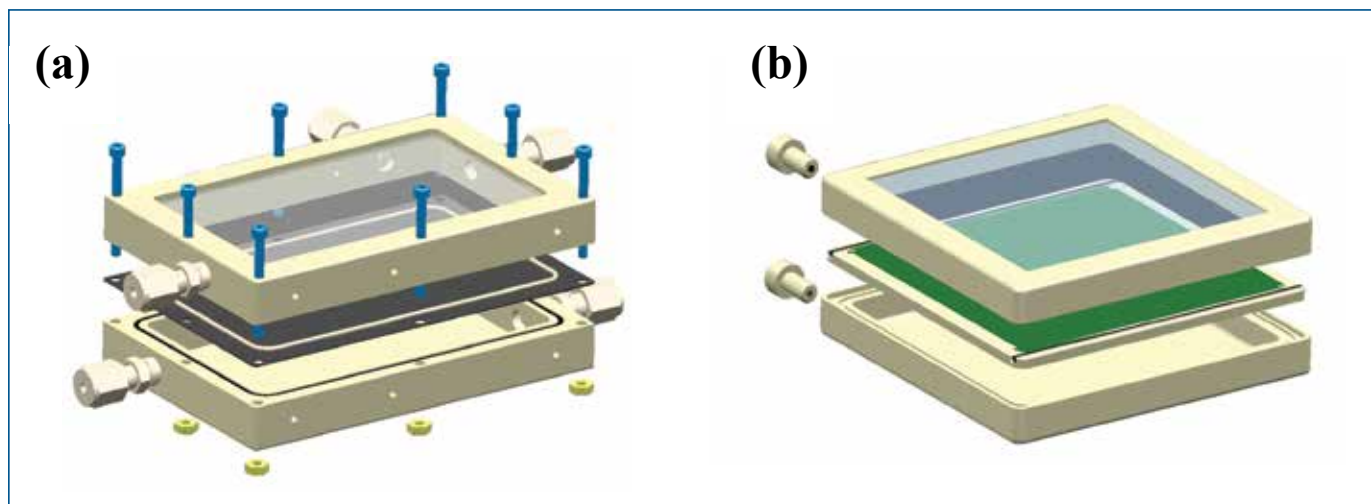

(a)   **(b)**

FIG. 7. *Schematic illustrations of (a) a prototyping engineering model for design evaluations, (b) a prototyping design that integrates light absorbing materials and membranes.*

Optionality in fuels produced.—A final emphasis of a balanced global R&D program on solar fuels generator systems should be to retain flexibility in the types of fuels that can be produced from sunlight. In one embodiment, water is split into H_2 and O_2, but H_2 is not necessarily the fuel that will be provided to the end-user. The H_2 could be converted into a liquid fuel by upgrading biofuels, for example, or could be combined with CO_2 from flue gas or otherwise using the reverse water-gas shift reaction, in conjunction with Fischer-Tropsch reactions, to produce liquid fuels for use in transportation applications, for example. An alternative is to directly reduce CO_2 to methanol or methane, for example.[30] R&D should also therefore be devoted to developing, discovering, and studying catalysts that can promote the six-electron and eight-electron reduction of CO_2 to methanol or methane, respectively. This process is envisioned as one in which the prototypes will have the optionality to produce either gaseous or liquid fuels, so that when the catalyst development program matures, the prototypes will already be developed and will be ready to receive this enhancement in functionality.

Summary

The development of a complex system, such as a solar fuels generator, requires much more than just the discovery of a catalyst, or of a photocatalyst, or even of a water-splitting nanoscale construct. It requires a full macroscale object that is embedded in, and forms the basis for, an article of manufacture that can be made at scale, and that can operate safely, cost-effectively, and efficiently over all length and time scales of interest. A highly integrated effort, involving individual research groups, teams of research groups, centralized, focused R&D efforts, and global cooperation is therefore important to realize this goal in a cost-effective, time-effective, and effort-effective fashion. This realization is the most compelling, and in fact the overriding, justification for a systems level approach to the successful development of a technology that enables the direct production, in a globally scalable fashion, of fuels from sunlight by artificial photosynthesis, to provide an important technology option in the pursuit of a globally scalable sustainable energy system.

Acknowledgments

About the Author

NATHAN S. LEWIS obtained his PhD in inorganic chemistry from MIT in 1981. He has been a Professor of Chemistry at Caltech since 1991; and Scientific Director of the Joint Center for Artificial Photosynthesis, the DOE's Energy Innovation Hub in Fuels from Sunlight, since 2010. His research interests include artificial photosynthesis and electronic noses. Dr. Lewis continues to study ways to harness sunlight and generate chemical fuel by splitting water to generate hydrogen. He is also developing an electronic nose, which consists of a chemically sensitive conducting polymer film capable of detecting and quantifying a broad variety of analytes. He may be reached at nslewis@caltech.edu.

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