Solar Fuel Production for a Sustainable Energy Future: Highlights of a Symposium on Renewable Fuels from Sunlight and Electricity

by Heli Wang, Deryn Chu, and Eric L. Miller

Synthesis of fuels from sunlight, water and carbon dioxide, without competing with food production, is an important route for sustainable development beyond fossil fuels. The magnitude of the challenge is very significant that requires scientific breakthroughs in materials and processing for creating economic opportunities.[1]

There are two straightforward conversion pathways for conversion of solar energy to fuels.[2] The most important one is the photoelectrochemical (PEC) hydrogen production via water splitting, which combines the electrical generation and electrolysis into a single system. The other pathway is replicating plant photosynthesis process with water and CO_2. These direct solar fuel pathways, especially the PEC water splitting approach, have attracted attention world-wide due to their renewable fuel generation and benefit to the environment. In electrochemical and photoelectrochemical techniques, the electrodes combine with catalysts, inhibitors, and an electrochemical flow reactor to convert CO_2 to organic fuels.

In PEC water splitting, the grand challenge of 10% solar-to-hydrogen (STH) efficiency and 10 year lifetime was defined as the "holy grail of chemistry."[3] The requirements for a successful PEC water splitting device is displayed in Fig. 1, as shown with a *p*-type semiconductor case. To achieve efficient PEC water splitting at an illuminated semiconductor (SC),

1. the band gap (E_g) of the SC must be at least 1.6-1.7 eV since the theoretical difference in equilibrium potentials between water splitting reactions is 1.228 V at 25 °C. The overpotential must be sufficient for water splitting reactions, but not over 2.2-2.3 eV in order to absorb the visible light;
2. the band edges of the SC must straddle the water redox potentials;
3. the SC must meet the need of efficient charge generation/transfer in the bulk and fast reaction kinetics at the interface; and
4. the SC must be stable in aqueous solutions.

It is challenging to develop materials that meet all the requirements of photoelectrodes/photocatalysts. To facilitate the research in photocatalysts and solar fuel production, a symposium on "Renewable Fuels from Sunlight and Electricity" was held at the 222nd ECS Meeting in Honolulu in October. Over 130 abstracts were received for this symposium. The symposium attendees came from North America, Europe, and Asia. The research theme of this symposium focused on the development of materials and devices for hydrogen generation and CO_2 conversion to fuels. One approach is to utilize the solar energy to produce fuels. Another approach is to utilize the electrical energy to generate fuels with electrochemical devices. The symposium presentations covered the following topics in both approaches:

- solar energy materials;
- photocatalysts;
- photo electrochemical cells (PECs);
- biological devices;
- solar concentrators;
- solid oxide electrolysis cells (SOECs);
- solid oxide fuel cells (SOFCs); and
- proton conductor electrolysis cells (PCECs) and fuel cells (PCFC).

In this paper, an emphasis is placed on the summary of the presentations for solar fuels production. We will highlight some of the presentations that reflected the research progress in this field.

Metal oxides are the most studied semiconductor material group. While metal oxides are more stable in aqueous solutions, key issues are wide band gap, band-edge mismatch and their intrinsic low STH efficiencies. A combinatorial screening might be a relevant approach to search for metal oxides with suitable band gap.[4] Different tandem cells[5-9] have been developed to solve the band edge mismatch. In the keynote speech, Akihiko Kudo at Tokyo University of Science (Japan) highlighted the *Z*-scheme type photocatalysts for water splitting with improved Rh-doped $SrTiO_3$ and $BiVO_4$. One the other hand, Lionel Vayssieres at Xi'an Jiaotong University (China) introduced an all-oxide quantum confinement approach to

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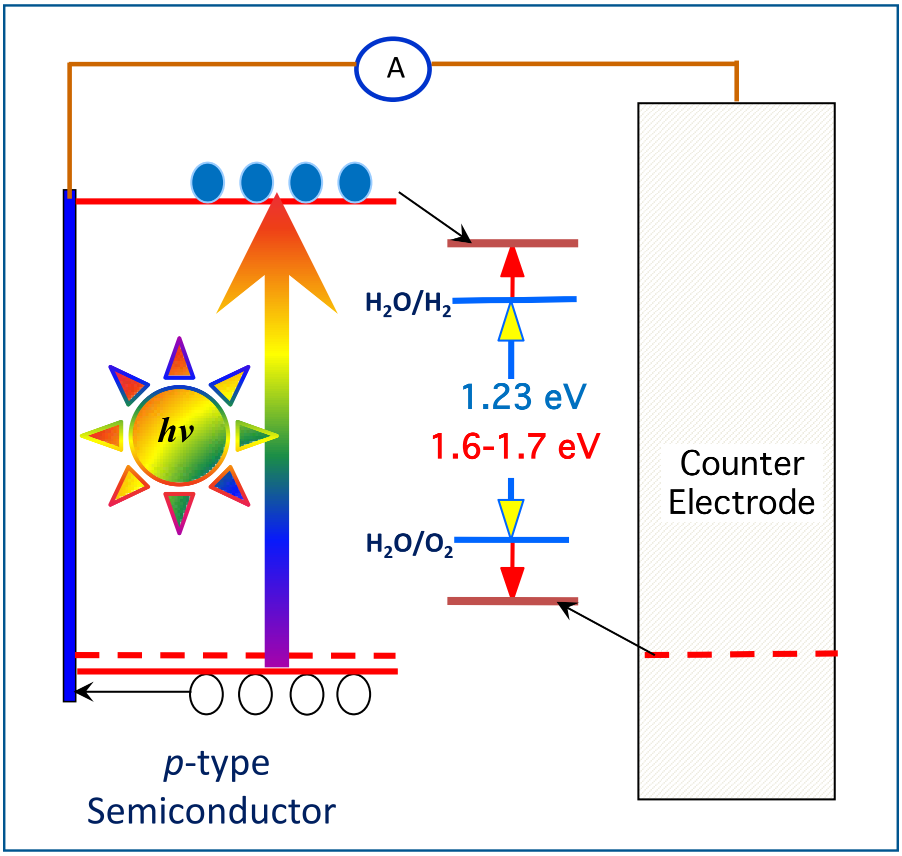

Fig. 1. *Schematic of the PEC water splitting process at illuminated p-type semiconductor.*

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solve the issue. The low solar-to-hydrogen efficiency is related to wide band gap, light absorption, charge mobility, recombination, interfacial kinetics, etc. To overcome this hurdle, different approaches have been discussed at the symposium, including band gap engineering, doping and co-doping, nanostructuring, and catalyst, etc. Moreover, Nam-Gyu Park at Sungkyunkwan University (Korea) presented new solar energy materials and nanostructures in his keynote talk.

Semiconductor materials such as III-V and I-III-VI_2 compounds have suitable band gaps and high efficiencies. The band edge mismatch was successfully solved by a tandem cell design.[10] However, the trade-off is the photo-corrosion of III-V materials in PEC hydrogen generation. Silicon materials have oxidation issue in the dark, thus eliminating continuous application. Naturally the surface modification and protection of the high efficient semiconductors have been discussed in the symposium. In the keynote speech, John A. Turner, the National Renewable Energy Laboratory (U.S.), addressed the competition of PEC hydrogen production *vs*. photovoltaic (PV) electrolysis, and delivered cost and economic considerations in selecting PEC materials.

Krishnan Rajeshwar, University of Texas at Arlington (U.S.), after a short review on PEC efforts over generations, focused on the economic preparation of new families of metal oxides for water splitting and CO_2 reduction in his keynote speech. Moreover, characterization and theoretical approaches opened new windows for understanding the challenge and discovering new PEC materials. The combined synthesis-characterization-theory loop will be an effective way to approach the 10% STH efficiency and 10-year life challenge.[3]

Naturally, there is no single material that could meet all the requirements of photoelectrodes/photocatalysts for water splitting; and this has challenged the PEC communities for decades. Multi-junction cells, quantum dots, and plasmonic metals brought new opportunities for research and development of PECs and photocatalysts. For example, Nianqiang (Nick) Wu, West Virginia University, talked about the development of plasmonic nanostructures for enhancing the photocatalysis. Plasmonic nanostructures convert the solar energy to the plasmonic energy stored in the oscillating electrons. Such energy can transfer from the metal to the semiconductor via a plasmonic-induced resonant energy transfer (PIRET) process,[11] leading to generation of electron-hole pairs in the semiconductor. The PIRET is an unprecedented mechanism of plasmon-enhanced photocatalysis, which provides the guidelines for development of plasmonic photosensitizes for solar energy harvesting devices.

Government support plays a key role to foster PEC R&D. In his keynote talk, Eric Miller of the Fuel Cell Technologies Program at the Office of Energy Efficiency and Renewable Energy of DOE (U.S.) shared the "big picture" of the roles of hydrogen and fuel cells in diverse energy portfolios. He illustrated the promises and challenges of different renewable solar hydrogen technologies, and addressed the need for national and international collaborations for leveraging research to meet these challenges. He presented the techno-economic analysis, indicating the critical need for materials systems with conversion efficiency exceeding 10% STH efficiency (in many cases, even exceeding the 20% mark) to meet the DOE hydrogen cost threshold.[12] This pushes the bar even higher for the solar-to-hydrogen materials researchers. Significant research progress has been made in the past four decades, efforts are still needed to design and explore new photocatalysts and PEC materials to meet the "holy grail" challenge.[3]

In CO_2 reduction, the thermodynamically uphill nature of this reaction, coupled with the large activation energy associated with the multi-electron and multi-proton reduction, makes the conversion of CO_2 a big challenge.[13] Thomas F. Jaramillo from Stanford University observed a total of 16 different CO_2 reduction products (C_1-C_3) from a polycrystalline copper electrode, five of which were presented at the meeting. They have expanded their studies to numerous metals such as Pt, Au, Ag, Ni, Zn, and Fe, as well as non-metal surfaces. Andrew Bocarsly from Princeton University presented the pyridinium catalyzed electrochemical reduction of CO_2 to methanol at illuminated p-GaP photocathodes; with Faradaic efficiencies exceeding 95%. From this effort, they proposed that the reduction of CO_2 is initiated by a mediated charge transfer process, in which the one electron reduction of pyridinium leads to the formation of a carbamate intermediate. Protonated imidazole was also found to be an active catalyst for the conversion of CO_2 to CO and formate in an aqueous electrolyte at an iron pyrite electrode.

Paul Kenis' group from the University of Illinois at Urbana-Champaign has developed an electrochemical flow reactor for CO_2 reduction, in which the anode and cathode are separated by a flowing liquid electrolyte (Fig. 2). Owing to the differences in binding energy of intermediates by different particle size, the reaction rate for CO_2 reduction increases upon the catalyst particle size decrease from 200 to 5 nm, but then decreases upon the particle size decreasing further to 1 nm. A thin, uniformly distributed, and agglomerate-free catalyst layer is a key because it eliminates mass transport issues while avoiding hydrogen evolution on bare carbon in the underlying gas diffusion

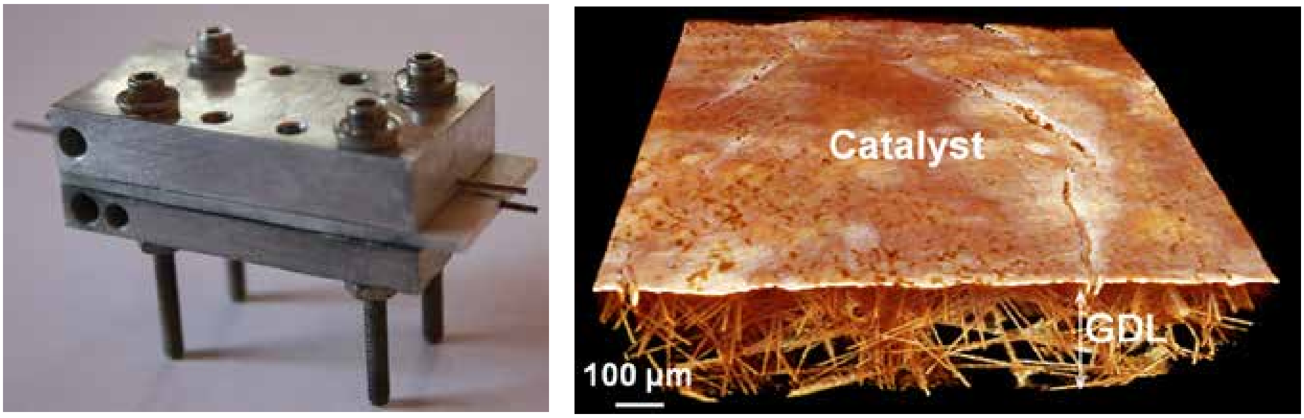

Fig. 2. *(Left) Photo of the electrochemical flow reactor for the electrochemical reduction of CO_2. (Right) Micro-computed 3D tomographic image of the air-brushed cathode for the electrochemical reduction of CO_2 to CO that shows the thin uniformly distributed catalyst layer.*

layer. The various optimization steps of the catalyst and the catalyst layer structure have led to current densities as high as 91 mA/cm^2 (with 94% selectivity for CO) while *at the same time* maintaining energy efficiencies that exceed 42%. These advances will help electrochemical CO_2 conversion to become an economically feasible process.

In his keynote presentation, Anil Virkar from the University of Utah highlighted a reversible solid oxide electrolysis cell (SOEC), which produces fuel in times of available electrical energy and consumes fuel to produce electrical energy in times of demand, as a chemical energy storage tool. In the SOEC configuration, electrical energy is used to electrochemically convert water and air to hydrogen and oxygen. Carbon monoxide and/or carbon dioxide may be incorporated to produce a syngas or hydrocarbon fuel. During this presentation, Prof. Virkar addressed the tendency for more severe degradation in electrolysis mode (fuel generation) by posing the fundamental question of if a perfectly insulating electrolyte is desired, or if rather a mixed ionic electronic conductor (MIEC) might provide some benefit. He highlighted that the potential for degradation might be mitigated by introducing some level of electronic conduction in the electrolyte, while achieving a high overall ionic transport number by suitably designing the interfaces.

Electrochemical reduction of CO_2 to small organic molecules is a very promising approach for generating useful fuel in the future. A series of fundamental research and development programs are ongoing at the United State Department of Defense. The Defense Advanced Project Agency (DARPA), Defense Science Office, initiated a program "Convert CO_2, Sunlight, and Water to Syngas" in 2008 under the "Surface Catalyst for Energy Program." The performers are the University of San Diego and the California Institute Technology. The University of San Diego also is leading a program to explore and develop this technology under the Air Force Research Office's Multi-University Research Initiative (MURI) program. The U. S. Army also initiated a "CO_2 Reduction to Fuels" Program in 2013. The U.S. Army Research Laboratory (ARL) and the U.S. Army Communication Electronic Research and Development Center (CERDEC) are collaborating with the University of Southern California (USC) and the West Virginia University for this technology. The electrochemical and photo-electrochemical conversion of CO_2 to small organic molecules as fuels has great potential to become a viable and economical technology.

About the Authors

Heli Wang is a senior scientist at National Renewable Energy Laboratory. He was a postdoctoral researcher at Uppsala University in Sweden before joining NREL in 2001. His research interests are photoelectrochemical cells for hydrogen production, charge transfer at semiconductor/electrolyte interface, corrosion and protection, and PEMFC components and system contamination. He is the author or co-author of one patent and one book chapter, as well as over 40 journal publications. He may be reached at heli.wang@nrel.gov.

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References

1. U.S. Department of Energy: New Science for a Secure and Sustainable Energy Future, December 2008, http://science.energy.gov/~/media/bes/pdf/reports/files/nsssef_rpt.pdf.
2. J. A. Turner, *Science*, **285,** 687 (1999).
3. A. J. Bard and M. A, Fox, *Acc. Chem. Res*., **28,** 141 (1995).
4. M. Woodhouse and B. A. Parkinson, *Chem. Soc. Rev*., **38,** 197 (2009).
5. A. J. Nozik, *Appl. Phys. Lett*. **30,** 567 (1977).
6. M. Grätzel, *Nature*, **414,** 338 (2001).
7. R. Abe, T. Takata, H. Sugihara, and K. Domen, *Chem. Commun.*, 3829 (2005).
8. H. Wang, T. Deutsch, and J. A. Turner, *J. Electrochem. Soc*., **155,** B99 (2008).
9. M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, and N. S. Lewis, *Chem. Rev*., **110,** 6446 (2010).
10. O. Khaselev and J. A. Turner: *Science*, **280,** 425 (1998).
11. S. K. Cushing, J. Li, F. Meng, T. R. Senty, S. Suri, M. Zhi, M. Li, A. D. Bristow, and N. Q. Wu, *J. Am. Chem. Soc.*, **134**, 15033 (2012).
12. U.S. Department of Energy Program Record 11007 (Offices of Fuel Cell Technologies): Hydrogen Threshold Cost Calculation, March 2011, http://www.hydrogen.energy.gov/pdfs/11007_h2_threshold_costs.pdf.
13. B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum, and C. P. Kubiak, *Ann. Rev. Phys. Chem.*, **63,** 541 (2012).