POWERING THE WORLD WITH SUNLIGHT

A White Paper Describing the Discussions and Outcomes of the 1st Annual Chemical Sciences and Society Symposium (CS3)

Kloster Seeon, Germany, July 23-25, 2009[1]

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[1] This white paper was prepared by science writer Leslie A. Pray, PhD, in consultation with the Gesellschaft Deutscher Chemiker e. V. and American Chemical Society, and reviewed by members of the CS3 Scientific Committee.

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EXECUTIVE SUMMARY

The sun provides more energy to the earth in an hour than the world consumes in a year. Compare that single hour to the one million years required for the earth to accumulate the same amount of energy in the form of fossil fuels. As the global population continues to expand and with life expectancies increasing worldwide, scientists estimate that total energy consumption of the world will more than double by 2050 if society continues to use energy at its current rate. Fossil fuels are not a sustainable resource, and we must break our dependence on them. Solar power is among the most promising alternatives. The challenge is: How can solar power be harnessed on the scale that is needed?

To initiate international cooperation and innovative thinking on solar solutions to the global energy challenge, thirty leading scientists from five national chemical societies[2], as well as representatives from the national science funding agencies of each country, convened in Kloster Seeon, Germany, in July 2009. The meeting was the first Chemical Sciences and Society (CS3) Symposium, a new annual series of symposia designed to bring top scientists together to discuss how the science of chemistry can provide solutions to some the world's most pressing challenges. The presentations, discussions, and outcomes of this first CS3 symposium revolved around the questions: How can solar energy be captured, converted, and stored on the scale needed? What are the most urgent scientific problems that must solved before solar energy can be used to meet the world's energy needs?

The international and interdisciplinary nature of the CS3 symposium set a new paradigm for the cross-fertilization of ideas that will be necessary for harnessing the power of the sun. The nearly unanimous agreement on many of the issues among an international group of experts specializing in different areas of the chemical sciences, many of whom had never met before, made a powerful statement about the readiness of the international chemistry community to seek a solar solution to the global energy needs of the 21st century.

Equally important, it became clear that national and international energy initiatives must make a stronger commitment to the central role of chemistry in realizing the potential of solar energy. This is because the conversion of energy from one form to another almost always involves a chemical reaction, and understanding the molecular nature of those chemical reactions is vital to developing new materials and processes that can be used to drive those reactions in affordable, sustainable ways.

While several overarching themes emerged over the course of the two-and-a-half day dialogue, CS3 participants identified the three key take-home messages:

- ***The science of today is the technology of tomorrow***: There is no single best solution to the energy problem. Science and society must seek more affordable, sustainable solutions to the global energy challenge by examining and considering all next-generation options. It is difficult to predict how scientific breakthroughs and emerging technologies being explored today will advance in the future.

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[2] The Chinese Chemical Society; Gesellschaft Deutscher Chemiker e. V.; Chemical Society of Japan; Royal Society of Chemistry; and American Chemical Society. The meeting was supported by the national science funding organizations of the five countries: National Science Foundation of China; German Research Foundation; Japan Society for the Promotion of Science; British Engineering and Physical Sciences Research Council; and U.S. National Science Foundation.

- ***Investing in chemistry is investing in the future***: Having a strong basic research program in chemistry is indispensable to realizing the potential of solar energy. The discovery of new materials and the design of new processes will be vital to making solar energy an affordable option for large-scale use.

- ***The chemistry students of today are the energy scientists of tomorrow****:* Society needs a new generation of energy scientists -- young minds eager to explore innovative ways to capture, convert, and store solar energy. Developing and optimizing solar energy technologies for large-scale use will be a long-term effort. Efforts should be made to encourage young investigators to address the wide range of scientific challenges that must be met before the tremendous potential of solar energy can be realized.

Research Recommendations

While silicon-based photovoltaic (PV) cells are the most common way of using solar energy, the high cost of purified silicon limits its widespread use. No matter how efficient an energy conversion technology is, much of the world will not be able to use it unless it is also affordable. During the final wrap-up session of the symposium, CS3 participants discussed the major scientific challenges and priority research goals in four areas of solar energy science. Almost all of the goals revolve around the need to develop not just efficient but also affordable solar energy technologies:

(1) *Converting solar energy into chemical fuel*: Artificial photosynthesis is any process that converts solar energy into chemical energy, mimicking what plants do during natural photosynthesis. Before artificial photosynthesis can become an affordable, sustainable solution for widespread use, chemists must:

- ***develop chemical catalysts for the two major processes of artificial photosynthesis -- water splitting and*** CO_2 ***reduction -- that can be applied commercially and are made of affordable, earth-abundant materials; and***

- ***create an "artificial leaf" by coupling water splitting and*** CO_2 ***reduction in a way that eliminates the need for an external, sacrificial electron donor.***

(2) *Accessing solar energy that already exists in nature*: Biofuels derived from non-crop biomass allow access to the enormous reservoir of solar energy that has already been naturally converted into plant mass. Before biofuel production can become an affordable, sustainable source of energy for widespread use, chemists must:

- ***develop biochemical methods that can be used to create more biomass; and***

- ***develop catalytic processes that improve the efficiency of biomass conversion.***

(3) *Converting solar energy into electricity*: The widespread use of silicon-based photovoltaic (PV) cells, which convert solar energy directly into electricity, is limited by their high cost. Before PV cells can become an affordable, sustainable mode of energy, chemists must:

- ***develop low-cost, non-toxic, earth-abundant PV materials for use in next-generation PV cells.***

(4) Storing newly harnessed and converted solar energy: We must develop systems that not only convert solar fuel into other forms of energy but also store that converted energy for future use. This is an especially critical issue for areas of the world without access to centralized energy delivery systems. Before low-cost, sustainable solar storage systems can be built, chemists must:

- ***develop new catalysts and materials from low-cost, earth-abundant elements that can be used to build affordable, sustainable solar energy transformation-and-storage systems.***

About this White Paper

This white paper summarizes the main issues and outcomes of this year's CS3, with an emphasis on the four areas of solar energy science listed above: Chapter I focuses on the conversion of solar energy into chemical fuel (i.e, water-splitting and CO_2 fixation), chapter II the conversion of biomass into biofuel, chapter III the conversion of solar energy into electricity (i.e., PV, or solar cells), and chapter IV the storage of solar energy. The CS3 program is attached as Appendix A and the list of participants as Appendix B. This paper should not be viewed as a comprehensive report of the many technical details addressed during the course of the 2-1/2 day workshop, nor does it cover all comments made by CS3 participants.

I

CONVERTING SOLAR ENERGY INTO CHEMICAL FUEL: IF A LEAF CAN DO IT, WE CAN DO IT[3]

Plants use solar energy all the time -- they capture and convert light into chemical fuel through photosynthesis. In chemical parlance, photosynthesis is the conversion of water (H_2O) and carbon dioxide (CO_2) into carbohydrates (CH_2O) and oxygen (O_2). The actual conversion comprises several separate reactions, the two main ones being the splitting of water into hydrogen (H_2) and oxygen ("water splitting") and the reduction of CO_2 using electrons released during the water splitting ("CO_2 reduction"[4]). The question is, can chemists replicate what plants do naturally?

Chemists have in fact mimicked most of what is required to make these separate reactions proceed. In essence, they have replicated photosynthesis. But it hasn't been easy, and chemists have yet to replicate the separate reactions in an integrated fashion and in a way that can be commercially applied on a wide scale. For example, as described below, scientists have only recently developed an experimental O_2 production reaction that is potentially affordable enough for widespread use; most current commercial O_2 production methods rely on the use of expensive platinum catalysts.

Most of the CS3 discussion on the conversion of solar into chemical energy revolved around current research efforts aimed at developing affordable catalysts for driving the various photosynthetic reactions forward. This chapter summarizes that discussion.

Developing Catalysts for Hydrogen Production

Dr. Kazunari Domen of the University of Tokyo, Japan, opened the session by describing current research efforts focused on developing more efficient and more affordable H_2 production catalysts using a new type of water-splitting technology: "photocatalytic overall water splitting." The technology makes use of nanostructured photocatalytic particles dissolved in solution, whereby the catalytic reactions and production of H_2 and O_2 occur in contact with these particles. This is different from conventional approaches, which use separate catalytic-coated electrodes for H_2 and O_2 production. The key advantage of photocatalytic overall water splitting is its reliance on less expensive materials than PEC cells require. Therefore, it can be more affordably scaled up for widespread use.

But first, Domen described the two conventional water-splitting technologies. The first involves the combined use of a photovoltatic (PV) cell (often called a "solar cell" or simply "PV"; see chapter III) and an electrolytic device, whereby the PV absorbs and converts the light energy into electricity and the electrolytic device uses that electricity to split the water. He

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[3] This section summarizes the presentations and discussions that took place during the first session of CS3, "Artificial Photosynthesis, Photocatalytic Water Splitting, CO2 Fixation," which was organized by Dr. Haruo Inoue, Tokyo Metropolitan University, Tokyo, Japan.

[4] A reduction reaction requires an electron donor. In natural photosynthesis, water serves as the electron donor.

mentioned that Honda has been using the first approach for several years in an effort to develop an experimental "solar-powered water-electrolyzing hydrogen station" where hydrogen fuel-operated cars could re-energize. The second approach involves the use of a photoelectrochemical (PEC) cell, a device that contains both the PV cell and electrolytes in tandem. By combining the light-harvesting and water-splitting processes in one device and eliminating the need for a separate electrolyzer, PEC cells provide a more direct, less expensive means of using solar energy to drive the water-splitting reactions. Domen pointed to several examples of the second approach.

Both conventional approaches are further advanced than photocatalytic overall water splitting, which Domen said is still very much in the research phase and not yet ready to be developed for any sort of commercial application. Chemists have built PEC cells, for example, with about 5% solar energy conversion efficiency. Photocatalytic overall water splitting systems, on the other hand, are only about 1 to 3% efficient at best. Domen predicts that it will take another 10 years of research to increase their average solar energy conversion efficiency to 5%. One of the key challenges is that most of the photocatalytic materials work only when activated by ultraviolet (UV) light, not visible light.[5] He described current efforts by his and other research groups to develop new materials that work efficiently under visible light. For example, after experimenting with a range of metal oxide materials, he and his collaborators have demonstrated good photocatalytic activity using a mix of gallium nitride (GaN) and zinc oxide (ZnO).

Following Domen's talk, there were several additional comments on some of the technical details of H_2 production. Dr. Haruo Inoue of Tokyo Metropolitan University, Tokyo, Japan, discussed the molecular details of how the electrons used in H_2 production are actually obtained from water during the water-splitting process. He argued that a two-electron oxidation approach to photochemical water splitting may be more promising than either a single-electron or multiple-electron approach to developing an artificial photosynthetic system that uses water as the electron donor (i.e., instead of an external, sacrificial electron donor). Dr. Chen-Ho Tung and Dr. Can Li, both of the Chinese Academy of Sciences, China, discussed some of the detailed chemistry of the H_2 production component of water splitting.

Developing Catalysts for Oxygen Production

In the following session on biomass (see Chapter II) but of relevance to water splitting, Dr. James Barber of Imperial College London, UK, briefly reviewed some of the history of chemical research on water splitting, beginning with work in the late 1960s by Bessel Kok. Understanding the basics of water splitting – for example, precisely where and how the O_2 molecules are formed – has been the subject of intense study for decades. He then described his team's recent discovery of the first complete structure of one of the key protein complexes involved in water splitting and the site of O_2 formation, photosystem II (PSII). They identified both the shape and manganese (Mn) and calcium (Ca) content of PSII, finally giving scientists a glimpse at catalytic machinery that has been operating on the planet for the past 2.5 billion years.

As both Barber and, later during the symposium (see Chapter IV), Dr. Daniel Nocera discussed, Barber's discovery of the structure of PSII also guided Nocera and his research group at the Massachusetts Institute of Technology (MIT), Cambridge, Mass., U.S.A., in their

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[5] While some sunlight is within the UV range (<400 nm), most solar light is visible (400-800 nm).

development of an artificial water-splitting system based on a novel cobalt-based O_2 production catalyst. Nocera's group demonstrated that by placing cobalt (Co) ions and potassium phosphate in solution with an indium tin oxide electrode and applying an electrical current, they were able to not only produce O_2 but to do so continuously. When a current is run through the solution, the cobalt, potassium and phosphate accumulate on the electrode and form an amorphous catalyst that drives the oxygen production component of the water-splitting reaction, forming oxygen gas (O_2). Hydrogen (H_2) is produced at a separate, platinum-coated electrode[6].

Nocera noted the "striking" similarities in both catalytic function and self-assembly between the cobalt catalyst and the naturally existing Mn-based PSII protein complex. The two complexes share the same basic structure except that the synthetic catalyst contains cobalt instead of manganese. Importantly, the synthetic catalyst can self-assemble (and re-assemble), eliminating the need to add additional raw material as the water splitting proceeds and the need to dispose of used reagent at the end of the reaction. So the catalyst continuously breaks down, but it also continuously builds back up, just like PSII; PSII is not very stable, with plants making repairs about every 30 minutes.

While the water splitting demonstrated by Nocera's group is not a new achievement in and of itself, the use of an inexpensive (i.e., non-platinum) catalyst for at least, in this case, the O_2 half-reaction, is remarkable. Nocera stated that if chemists could develop an affordable, efficient means of using solar energy to split water and produce hydrogen fuel, society would be able to power the world simply by splitting, every second, one-third the amount of water in MIT's swimming pool. That is a compelling image.

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Self-Healing: A Desirable but Elusive Quality

Of relevance to Nocera's emphasis on the importance of self-assembly, Dr. Kazuhito Hashimoto, University of Tokyo, Japan, commented during this session on two desirable aspects of any next-generation PV technology, indeed any type of solar energy technology: (1) the ability to self-assemble or self-organize and (2) the ability to self-heal. Noting that natural photosynthesis is typically only 4 ½-5% efficient at best (see Chapter II), Hashimoto argued that most artificial systems are already "better" than natural photosynthesis with respect to solar energy conversion efficiency. Clearly, however, artificial systems are lacking something that nature has – specifically, the ability to self-assemble *and* the ability to self-heal. Hashimoto described a paddy-field power generation system that uses "microbial fuel cells" (bacteria that can convert biomass into electricity) to convert stored carbohydrates into electricity. Under the right conditions, the solar-to-electricity paddy-field power generation system can survive on its own, thereby satisfying the self-assembly criterion of a natural system. But he and his colleagues have yet to figure out how to build a self-healing system. The solar energy conversion efficiency of the system is only about 0.3%, although Hashimoto said that it could probably be improved ten-fold by improving some of the technical components.

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[6] When asked about the hydrogen catalyst component of his new water-splitting system, Nocera mentioned that he and his team have developed a nickel alloy-based electrode to replace the prohibitively expensive platinum-based electrode typically used, but they have yet to determine whether it performs as well or better.

Building an "Artificial Leaf": Coupling Water Splitting and CO_2 Reduction Artificial Photosynthesis

Domen stated that the ultimate goal of artificial photosynthesis is to combine the water splitting and CO_2 reduction reactions, using the electrons released during the water splitting to drive the CO_2 reduction and produce a liquid fuel, such as methanol. Achieving this would, in essence, fulfill the vision of creating an "artificial leaf" – a device that not only splits water but also uses the products of the water-splitting reaction to create a more usable organic fuel, mimicking what real leaves do.

As Dr. Haruo Inoue, Tokyo Metropolitan University, Tokyo, Japan, explained, coupling CO_2 reduction with water splitting would be an ideal system from both an energy conversion and "circulation-of-elements" perspective. An artificial leaf would neither require energy (i.e, other than what it gathers from the sun) nor emit CO_2. CO_2 reduction does not have to be coupled with water splitting in order to be used for fuel production. Unfortunately, however, the major source of H_2 used in most CO_2 reduction processes that are currently in operation is the steam reforming of methane, which not only requires energy (i.e., currently in the form of fossil fuels) but also emits CO_2.

Dr. Etsuko Fujita of Brookhaven National Laboratory, Upton, New York, agreed that at least one overall goal of research efforts in the field of artificial photosynthesis should be to combine CO_2 reduction with water splitting. She laid out a vision for the future where CO_2 is captured at fossil fuel burning plants before being released into the atmosphere and then reduced using electrons (and protons) released during water splitting. There would be no need for a sacrificial electron donor. But the challenge is formidable. As both Fujita and Dr. Anthony Harriman, Newcastle University, United Kingdom, discussed, coupling the two halves of what makes a leaf a leaf would require joining together several complicated multi-electron reactions.

Meanwhile, until H_2 production can be coupled with CO_2 reduction, chemists are developing systems that use H_2 as an end product. For example, Nocera described how his cobalt-based O_2 catalyst could be integrated into a larger PV-and-fuel-cell system for hydrogen fuel production and storage: the H_2 produced from the water splitting would be used as a fuel (i.e., in a fuel cell, where it is would be combined with O_2 to release energy), and CO_2 reduction would not be part of the process. As a first step toward realizing this vision, Nocera is collaborating with Sharp Electronics to see if the system can be integrated with Sharp's PV technology.

Catalysts for CO_2 Reduction

As Dr. Koji Tanaka, Institute for Molecular Science, Okazaki, Japan, and others discussed, building an artificial leaf will require developing better catalysts not just for H_2 and O_2 production but also CO_2 reduction. In fact, Dr. Can Li of the Chinese Academy of Sciences, Beijing, China, suggested that "solving CO_2 reduction" is more urgent than "solving water splitting." Fujita agreed that, just as with H_2 and O_2 production, chemists have yet to optimize catalysis of the CO_2 reduction reaction. She commented on how both Dr. Osamu Ishitani's research group at the Tokyo Institute of Technology, Japan, and her research group have been working on the reduction of CO_2 for the past 20 years. Ishitani's team recently developed a novel ruthenium (Ru)-rhenium (Re) photocatalyst, but challenges remain. For example, the CO_2

reduction takes a lengthy ten hours, owing to the extreme stability of CO_2 molecules and the instability of the catalyst. Another problem, Li said, is that often the final hydrocarbon product of CO_2 reduction is very quickly re-oxidized, making the net hydrocarbon yield quite low. He emphasized the need to study natural systems in an effort to better understand how this can be avoided.

CO_2 Reduction: Not for Fuel Alone

Whether coupled to water splitting or not, CO_2 reduction has other uses besides fuel production. In fact, CO_2 is often used as a raw material for the production of a wide range of non-fuel products, including urea (an important component of nitrogen fertilizers), salicylic acid (a pharmaceutical chemical), cyclic carbonates, ethylene and propylene polycarbonates, and polyurethanes. It has been proposed in the past that the chemical industry, through its use of CO_2 as a chemical feedstock, might be able to contribute to lowering the level of CO_2 in the atmosphere by using more CO_2 during manufacturing. However, as both Fujita and Dr. Walter Leitner of the Institute for Technical and Macromolecular Chemistry, Aachen, Germany, discussed, the scale of CO_2 consumption is small compared to the total annual CO_2 emissions. The chemical industry uses the equivalent of less than 0.5% of total anthropogenic CO_2 emissions. Moreover, many polymeric products that could potentially be manufactured using CO_2 as a starting material would need to be made more durable before their production could be scaled up. Clearly, Fujita argued, we cannot rely on CO_2 utilization by the chemical industry to significantly mitigate CO_2 emissions from fossil fuel burning.

Leitner suggested that, because CO_2 utilization by the chemical industry cannot significantly mitigate the CO_2 emissions from fossil fuel burning, the question is not “How much CO_2 are we going to fix?” Rather, the question is, “What is the difference between using CO_2 as opposed to some other starting material to make a product?” Efforts should be re-directed toward thinking about the value added when CO_2 is used as a chemical feedstock and away from thinking about how using CO_2 as a raw material can mitigate CO_2 emissions.

Converting Solar Energy into Chemical Fuel

Artificial photosynthesis is any process that converts solar energy into chemical energy, mimicking what plants do during natural photosynthesis. What must be achieved before artificial photosynthesis can become an affordable, sustainable solution for widespread use? During the final wrap-up session of CS3, a breakout group identified the following as the most pressing scientific challenges:

Develop chemical catalysts for the two major processes of artificial photosynthesis -- water splitting and CO_2 reduction -- that can be applied commercially and are made of affordable, earth-abundant materials.

Create an “artificial leaf” by coupling water splitting and CO_2 reduction in a way that eliminates the need for an external, sacrificial electron donor.

II

ACCESSING SOLAR ENERGY STORED AS BIOMASS[7]

In his opening presentation of the second session of CS3, Dr. James Barber of Imperial College London, UK, described the planet as a "macroscopic reaction vessel" driven by a photosynthetic process that has been going on for 2.5 billion years. None of the plant mass on earth, nor the fossil fuels stored beneath the surface of the earth, would exist as they do today without photosynthesis -- that is, the conversion of solar energy into carbohydrates. While many countries are already tapping into this vast resource of already existing and naturally converted solar energy, there is considerable uncertainty and debate around the extent to which fuels derived from plant biomass ("biofuels") can meet the world's energy demands. Much of the CS3 discussion on biofuels revolved around this uncertainty, as well as on ways to improve biofuel production. This chapter summarizes that discussion.

Are Biofuels a Solution?

CS3 participants agreed that biomass can only be a part of the solution to the global energy challenge. As Barber explained, its use is limited by two related factors. First, natural photosynthesis is a relatively inefficient process, with most plants unable to convert more than, at best, about 4.5% of absorbed solar energy into carbohydrate fuel. (Following Barber's talk, there was some discussion about the optimism of 4.5%, with a couple of CS3 participants suggesting that most plants' solar energy conversion efficiencies are much lower. Not only is much of the light that hits a plant reflected [and therefore not absorbed], but also the photosynthetic process becomes saturated at very high light intensities. Barber explained that the 4.5% figure is a maximum and that solar energy conversion efficiencies vary over time and among plants. For example, the conversion of light energy into chemical bonds is much higher during rapid growth, with plants accumulating biomass more quickly at certain times. Additionally, some plants accumulate more biomass than others under a given amount of light simply because of their genetic makeup.) Solar energy conversion efficiencies of biomass crops would need to be increased, for example through genetic or biochemical engineering, before biofuels can become a more widespread practical solution.

Second, fuel biomass requires land. The rate at which light energy is converted into chemical bonds in terrestrial biomass amounts to the equivalent of about 100 terawatt-hours (TWh[8]) per year. Barber remarked that this is not very much, considering that the world uses about 14 TWh per year, a rate that is expected to more than double by 2050. He said that it is unrealistic to expect that, by 2050, one-third of the total land biomass on earth could be

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[7] This section summarizes the highlights of the presentations and discussions that occurred during the second session of CS3, "Solar Radiation to Energy via Biomass," which was organized by Dr. Laurie Peter, University of Bath, UK.

[8] A terawatt (TW) is the same as one trillion, or 10^{12}, watts. A terawatt-hour (TWh) is a measure of total energy used over time.

harvested for biofuel production. Again, this points to the need to improve the solar energy conversion efficiency of fuel biomass.

While biofuel production may not be a practical global solution, CS3 participants agreed that biofuel production serves as a good local or regional solution in some circumstances. For example, Brazil has been successfully converting sugarcane (*Saccharum* sp.) into bioethanol for the past several decades. Today, sugarcane-derived biofuel provides about one-third of Brazil's total energy, and about half of all cars sold in Brazil operate with a bioethanol-gasoline blend. The United States, on the other hand, relies on biofuel, most of which is corn (*Zea mays*)-based, for only about 3% of the country's energy needs. While the U.S. Department of Energy has predicted that this figure could increase to 30% in the future, Barber explained that there are several caveats to this prediction. For example, it is not clear whether there would be enough available (or dedicated) landmass to achieve that level of biofuel production.

Whether biofuel production is a practical global solution or not, bioethanol production is increasing worldwide. For example, Barber commented on a northern Italian plastics company that has demonstrated the capacity to grow 5 to 10 tons of dry matter per hectare (by growing one crop in winter and a second crop in summer), which according to the company's predictions would yield about one ton of bioethanol per hectare. Barber emphasized that the bottom line for a company is not efficiency but cost and whether production will yield a profit. In this case, the company has decided that the amount of biomass that they can grow and the rate at which they can convert it into biofuel is sufficient to earn a profit. (Following Barber's presentation, there was a question about whether the one-ton figure might be overly optimistic and whether factors such as the amount of fertilizer and water and the energy required for harvesting had been included in the calculations. Barber stated that the company had taken these factors into consideration. Hopefully, he remarked, biofuel crops of the future will have fewer energy demands than those being used today.)

Following Barber's presentation, there were a couple of comments about biofuels not being a global solution but nonetheless playing unique role in the energy field. Dr. Mark Davis of the U.S. National Renewable Energy Laboratory (NREL), Golden, Colorado, commented on their suitability as a liquid fuel for transportation applications. He said that other solar technologies, like photovoltaic (PV) cells, will probably figure more prominently in electrical production, but it is difficult to conceive that PV cells and some of the other technologies being developed are going to be useful for producing liquid fuels. Dr. Ferdi Schüth of the Max Planck Institute für Kohlenforschung, Mülheim, Germany, stated that while there are many exaggerated claims about the extent to which biofuels can help meet the energy demands of the world and while, to a large extent, much of our future energy system will probably be electricity-based, some of it will be material-based; biomass is one of the most readily available material-based fuels.

Ways to Improve Biofuel Production

Barber also discussed how the field must move forward in order to optimize biofuel production and produce biofuels on a scale that is competitive with fossil fuels. Most importantly, because fuel biomass often competes with food crops for land, scientists have proposed using the cellulose bioproducts of agriculture instead of the food itself for biofuel production. But in order for biofuel production to become cellulose-based, instead of food-based, scientists need to develop "energy crops" (i.e., non-food plants) and new agronomic practices for growing and harvesting those crops. For example, many chemists are studying the potential to use *Miscanthus*, a high-yielding grass, instead of corn (or another food crop) as a biofuel source. Additionally, chemists need to develop better organic and synthetic catalysts for converting cellulose into simple sugars and for converting those simple sugars into fuel products. As Barber explained, cellulose is a very complicated structure and is difficult to break apart. Some chemists are approaching the problem by investigating natural enzymes in termites and other pests and testing whether those same enzymes can be used in an energy conversion system.

In the discussion following Barber's talk, Davis agreed that better catalysts are needed for both the front end (breaking polysaccharides into smaller molecules) and the back end (building those smaller molecules back up into fuel products) of biomass conversion; better catalysts would reduce the amount of energy being used breaking and building chemical bonds. Davis also commented on the need to change some of the chemical processing steps of biofuel production in order to lower the cost of production and, therefore, the cost of biofuel. In sum, using different types of crops (e.g., *Miscanthus* instead of sugar or corn), developing better harvesting techniques, and changing some of the chemical processing steps would all contribute to bringing the cost down and making biofuel production more competitive with fossil fuels.

As an example of the type of work being done to build better catalysts for biofuel conversion, Dr. Michikazu Hara of the Tokyo Institute of Technology, Japan, commented on work that his research group has been doing with a particulate- and carbon-based solid acid catalyst for the conversion of cellulose into sugars. Unlike other acid catalysts that cannot be re-used and must be separated out and treated as waste when the reaction has been completed, his substance can be re-used in subsequent reactions.

While most of the CS3 discussion on biofuels focused on land biomass, Dr. Fang Huang of the Chinese Academy of Sciences's Institute of Botany, Beijing, China, commented on her research group's experiments with the use of microalgae as a biomass source for fuel.

Energy is a Systems-Level Issue

Davis' discussion of the cost of biofuel production led into a discussion about the importance of examining the full life cycle of biomass-to-biofuel conversion. That is, how much energy is required to produce biofuel? Which steps are the most costly in terms of energy loss? Where can improvements be made? Even in Brazil, despite decades of widespread use of bioethanol, the full life cycle of bioethanol is still unclear. CS3 participants agreed that the need to consider the full life cycle of an energy conversion process is true of all solar energy technologies, not just biofuels. Even with artificial photosynthesis, for example, when the technology matures it will be important to consider not just energy output but also the amount of energy required to build the devices and carry out the processes. Davis emphasized, however, that caution be taken when evaluating any lifecycle or systems-level analysis of solar energy conversion technologies, as the results are highly depending on which factors are considered and the assumptions of the analysis. Many life system analyses of biofuels are based on assumptions derived from corn, which involves fairly high-intensity agricultural practices. If those same assumptions are used when evaluating biofuels derived from a non-corn crop that is not as energy-intensive, the results may not be as favorable as they should be.

Use of Biofuels

Dr. Walter Leitner, Institut für Technische und Makromolekulare Chemie, Aachen, Germany, initiated some discussion on the use of biomass not just as a source of fuel but also as a source of added value. That is, products can be made from biomass than cannot be made using any other material. Biomass is already regularly used to produce high-value carbon-based chemicals, like high electrolyte oils used as lubricants or in the medical industry. Leitner reiterated that "first-generation" biofuels, namely ethanol (i.e., from sugar cane and corn) and biodiesel (e.g., from sunflowers and soy beans), are clearly not a sustainable solution except in certain regions. "Second-generation" biofuels -- that is, those that use liquid cellulose as a feedstock, as Barber and Davis discussed – are a better option because of their higher energy content and other factors. Still, Leitner said, they are not a global solution. Thus, he urged consideration of a "third-generation" biomass conversion approach, one that scientists at his research institution have adopted: the selective conversion of biomass into products that are specifically designed for their application. These tailor-made products can include fuels and fuel components, but they also include value-added chemicals, lubricants, pharmaceuticals, and other products – things that cannot be made using other technologies.

Accessing Solar Energy That Already Exists in Nature

Biofuels derived from non-crop biomass allow access to the enormous reservoir of solar energy that has already been naturally converted into plant mass. What must be achieved before biofuel production can become an affordable, sustainable source of energy for widespread use? During the final wrap-up session of CS3, a breakout group identified the following as one of the most pressing scientific challenges:

Develop biochemical methods that can be used to create more biomass[9].

Develop catalytic processes that improve the efficiency of biomass conversion[10].

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[9] The enzyme (known as "RuBisCO[9]") that takes CO_2 out of the atmosphere and incorporates it into plant biomass is very sluggish and does not discriminate well between CO_2 and O_2. Often, it grabs hold of O_2 instead of CO_2. Not only does a plant waste energy when RuBisCO makes this mistake, it wastes even more energy fixing the mistake. By improving RuBisCO's performance through protein engineering, chemists estimate that they could increase available plant biomass by at least 50%.

[10] The most abundant forms of biomass contain a high level of oxygen, and too much oxygen reduces the amount of energy available (per unit of biomass). Developing resource- and energy-efficient ways to remove oxygen from the complex molecules involved in biomass conversion would increase available biomass energy.

III

CONVERTING SOLAR ENERGY INTO ELECTRICITY: NEXT-GENERATION PHOTOVOLTAIC (PV) TECHNOLOGIES[11]

Photovoltaic (PV) cells ("solar cells") are devices that convert sunlight into electrical energy.[12] While photovoltaic PV technology is arguably the most popular type of solar technology in use today, with many people associating the notion of solar power with an image of solar panels on rooftops, it constitutes only a fraction of global energy production. According to Dr. Alvin Compaan, University of Toledo, Ohio, about 20 terawatts (TW) of electricity were produced worldwide in 2008. Only 7 gigawatts (GW) of that 20 TW (0.035%) were in the form of PV modules. Widespread use of PV technology is limited by the high cost of silicon. Most PVs currently being manufactured and used worldwide are made of solar-grade silicon (Si)[13]. Repeated calls were made throughout the course of the two-and-a-half-day CS3 for more affordable PV materials and manufacturing methods. In fact, scientists continue to develop and experiment with different semiconductor materials and solar cell structures. But they face some serious challenges. For example, while innovative organic molecule-based PV technologies are potentially much less expensive than silicon-based solar cells, the stability and longevity of the organic materials is a major concern. In this third session of the symposium, CS3 participants discussed the challenges and opportunities of several "next-generation" PV technologies. This chapter summarizes that discussion.

Overview of PV Technology: Chemists Look for Ways to Cut Cost

Dr. Junhao Chu of the Shanghai Institute of Technical Physics, Shanghai, China, opened the session with an overview of PV technology. PVs were among the first solar power technology developed, by Bell Lab scientists in the 1950s, and worldwide production has been increasing practically exponentially over the past decade. According to Chu, total worldwide production of PVs was about 125.8 megawatts (MW) in 1997, compared to 3733.4 MW in 2007. Chu predicted that the annual installation of PV power will continue to increase at a rapid rate in the near future, with a conservative estimate of more than 13,000 MV MW of solar power being generated in 2012.

The majority of PV production occurs in China, mostly for export. In 2008, about one-third (33%) of all PV production occurred in China, followed by Germany (21%), Japan (16%), Taiwan (7%), elsewhere in Europe (7%), elsewhere in Asia (7%), U.S.A. (6%), and India (1%). By 2011, China and Germany are expected to remain the leading two producers of PV

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[11] This section summarizes the highlights of the presentations and discussions that occurred during the third session of CS3, "Photovoltaics, Including Organic Solar Cels, Inorganic Solar Cells and Dye-Sensitized Solar Cells," which was organized by Dr. Chen-Ho Tun of the Chinese Academy of Sciences, Beijing, China.

[12] Illumination of a semiconductor material inside the PV device generates an electric current.

[13] Solar-grade silicon is different than pure silicon; among other differences, it is treated with chemicals that increase its electrical conductivity.

technology, accounting for 19% and 13% of all PV manufacturing, respectively, followed by Malaysia (11%). Even though China is the greatest producer of commercial PV technology, it uses very little of what is produced; its 2008 share of the global market was only 0.17%.

Chu emphasized that while there has been considerable rapid progress in PV production over the past several years, PV science and technology remains a very active area of research and innovation. Continued research and innovation will be essential to the development of more affordable materials. This is true even though the cost of solar-grade silicon has dropped, from \$350-400/kg in December 2007 to \$100/kg in December 2008. Silicon is still the most costly component of PV production, accounting for nearly 60% of the cost of producing a single solar cell module, or panel.[14]

Existing and Emerging PV Technologies

Chu described three different types of PV technologies:

(1) Crystalline silicon (c-Si) PV technology

Currently, c-Si technology dominates the marketplace, with about 87% of all solar array installations worldwide comprised of c-Si cells. However, there is ample room for improvement. Most importantly, while c-SI PV technology is the most efficient of all PV technologies (and, arguably, all solar energy technologies), with an average 15-20% efficiency of converting absorbed sunlight into electricity, the current cost of c-Si technology is prohibitively expensive for widespread use. Chu emphasized the need to continue to reduce the thickness of the silicon wafer that makes up such a large part of each first-generation c-Si PV cell. Although the average thickness of wafers has decreased in size more than 50% over just the past few years, from about 300-350 microns in 2003 to about 150 microns by 2010, it needs to be decreased even further in order to put the cost of the technology into a more affordable range.

While decreasing the wafer thickness makes good economic sense, it creates a new set of challenges. Specifically, it increases the chance that not all photons will be absorbed, with some being reflected back into the atmosphere, thereby decreasing the cell's solar conversion efficiency. Chu mentioned two ways that cells can be modified in an effort to avoid this problem: (1) "light trapping" and (2) improved surface passivation. Light trapping increases the amount of absorbed light that gets "trapped," for example by creating an inverted pyramid silicon surface or adding mirror-like metal layers to the back of the device. Passivation renders the surface of the semiconductor chemically and electrically "passive," thereby reducing its chemical reactivity and improving the likelihood that the charge carriers (i.e., the electrons and holes) will be transported into the external circuit. Chu showed a few examples of how these techniques have been used to make c-Si cells more efficient. For example, by adding passivating layers of SiO_2 to both the front and rear surfaces, Fraunhofer Institute for Solar Energy Systems (Fraunhofer ISE), Freiburg, Germany, developed a 21.6% efficient LFC-PERC (laser-fired contact -- passivated emitter, rear cell) solar cell. SunPower Corporation, San Jose, California, and Sanyo Electric Company, Moriguchi, Japan, have both used passivation techniques to reduce the cost and

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[14] A solar module, or panel, is an assembly of interconnected solar cells. It is the functional unit of most solar PV systems.

improve the efficiency of their respective proprietary c-Si PV technologies. SunPower has reported 21% efficiency, and Sanyo has reported 22.3% efficiency.

Chu also discussed some recent research on other materials besides SiO_2 that can be used for passivation. For example, researchers at RWTH Aachen University, Germany, have been studying the use of silicon nitride (SiN_x) as a passivating material; scientists at Applied Materials, Inc., Santa Clara, Calif., have been investigating passivation using a combination of SiO_2 and SiN_x; and researchers from Eindhoven University of Technology, Netherlands, the Institute for Solar Energy Research at Leibniz University, Hannover, Germany, and the Tokyo Institute of Technology, Japan, have been studying the use of aluminum oxide (Al_2O_3) films as a passivating material. To date, the "world record"[15] using such passivating materials with c-Si cells is Sanyo's reported 22.3% efficiency.

(2) Thin Film Solar Cells (TFSC)

Chu spent most of the remainder of his time discussing "second-generation" thin-film PV (TFPV) technologies, which include amorphous silicon (aSi)-based TFSCs as well as TFSCs comprised of other chemical compounds, such as polycrystalline copper indium (di)selenide (CIS), copper indium gallium (di)selenide (CIGS), cadmium telluride (CdTe), or epitaxial[16] layers of indium gallium phosphide (InGaP) and gallium arsenide (GaAs).

Most TFPV cells have relatively low efficiencies compared to c-Si cells, with typical efficiencies in the 10-13% efficiency range. Most TFPV production modules are about 5-10% efficient. However, as Chu discussed, there is wide variation in TFPV efficiency, which among factors depends on whether a cell is "multi-junction" or not. Multi-junction PV cells contain multiple layers of different semiconductor materials, with each type of material absorbing a different wavelength of light. Increasing the range of light wavelengths that can be absorbed increases the amount of solar energy that can be converted into electrical energy. Some multiple epitaxial layer cells (e.g., "triple junction" cells) have efficiencies greater than 40%. As just one example of new materials being explored for their use in multi-junction TFPV devices, Chu pointed to the use of gallium-indium-nitride-arsenide (GaInNAs) and boron-gallium-indium-arsenide-phosphide (BGaInAs) layers by scientists at the U.S. National Renewable Energy Laboratory, Golden, Colorado.

In addition to their lower efficiency (compared to silicon wafer PV cells), stability poses another key challenge for TFPV. Many thin-film solar cells are inherently unstable because their materials degenerate over time when exposed to light. As Chu explained, lack of stability can be materials-related (e.g., while CIGS is relatively stable, a-Si is susceptible to light-induced degradation), adhesion-related (i.e., peeling can occur between layers or from the substrate), or capsulation-related (i.e, moisture can penetrate the encapsulated module through laminated edges).

Despite their efficiency and stability drawbacks, thin-film solar cells require fewer raw materials and are less expensive to build than c-Si cells. They also have a shorter energy "payback" period. That is, all solar cell modules require energy to produce, but TFPV modules "pay back" that energy more quickly in terms of generated electricity compared to silicon wafer technology. It takes about four years for a typical wafer silicon cell to "pay back" all the energy that was required to make the cell in the first place, compared to only about one year for a thin-

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[15] "World record" efficiencies are for research laboratory settings; efficiencies in practical settings are usually lower.

[16] An epitaxial layer is a type of semiconductor layer with a particular crystalline structure.

film silicon-based solar cell. Added to their lower cost and shorter energy payback period, their flexibility and light weight make them suitable for applications not possible with the more conventional silicon wafer technology (e.g., for space, military, building-integrated installations).

While TFPVs are not as popular as c-Si PVs, a growing percentage of PV installations are thin-film based. For example, Chu mentioned a planned 1.3 MW (megawatt) power station being built in Germany using CdTe-based solar cells (the Dimbach Solar Park); and an amorphous silicon-based thin-film system on the roof of the Beijing New Capital Museum, Beijing, China, which provides 300kW of power using flexible panels developed by United Solar Ovonic, a subsidiary of Energy Conversion Devices, Rochester Hills, MN. By 2012, Chu predicts that 75% of all PV installations will be c-Si-based (down from the current figure of about 87%), the remaining 25% thin film-based.

More on Thin-Film Solar Cells

Following Chu's presentation, Dr. Alvin Compaan of the University of Toledo, Ohio, echoed Chu's comments about TFPV becoming a more popular choice in the future. In fact, Compaan stated that, in the United States, most silicon-based PV production is with thin-film, not wafer, technology (i.e., by Uni-Solar). Compaan mentioned three inorganic thin-film PV technologies that have reached large-scale manufacturing in the past four years: Ohio-based First Solar's cadmium telluride (CdTe) TFPV cells, Michigan-based Uni-Solar's amorphous-silicon TFPV cells, and Arizona-based Global Solar's copper indium gallium diselenide (CIGS) TFPV cells. At least one of these companies (First Solar) has experienced major cost breakthroughs as well.

However, many chemical challenges remain before some types of TFPV technologies can be advanced and other types can be scaled up for widespread use. Compaan mentioned two: (1) TFPVs made of polycrystalline materials pose the same type of passivation problem that some materials used in c-Si technology create, as Chu discussed. (2) While some TFPVs demonstrate relatively high efficiencies in research lab settings, their actual efficiencies following large-scale manufacturing are much lower. CIGS, for example, is a difficult material to manufacture and so, while CIGS TFPVs may be 20% efficient in the lab, actual modules manufactured for sale are less than 10% efficient.

Compaan then discussed in more detail his collaboration with First Solar and the future of CdTe TFPV technology. As with indium (which was mentioned following Chu's comments on organic molecule PV technologies – see below), there is concern about Te availability. In 2008, CdTe module production used a total of about 50 tons of Te, all of which came from copper (Cu) mine tailings.[17] Currently, Te is extracted from Cu tailings at only about 33% efficiency, yielding about 500 tons a year. If that extraction efficiency could be increased to 80%, Compaan explained, it would support about 25 GW of CdTe-based PV production a year.

Compaan also addressed concern about Cd toxicity, stating that most Cd emissions are indirect emissions produced during the coal-fired electricity generation needed for the module production process. Since the production of CdTe modules requires less electricity than the production of c-Si wafer modules, Cd emissions are actually quite low in comparison. When asked about recovery costs at the end of the lifecyle of a CdTe cell, Compaan stated that First Solar has set up an escrow account for every panel sold and which will be used for recycling all

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[17] There are some Te-enriched reserves in areas of China that are just beginning to be explored, but to date all Te is extracted from other mining operations.

old panels to make sure that the Cd is properly sequestered. Still, Dr. Dan Nocera of MIT commented on the "huge hidden costs" with CdTe technology.

(3) "New-concept" PV technologies, including dye-sensitized cells (DSC) and organic cells.

Chu mentioned three types of "third-generation" new concept solar cell technologies:

1. *Dye-sensitized solar cells (DSSC).* First engineered by Michael Grätzel in 1991, DSSC (also known as "Grätzel" cells) use dye molecules to absorb incoming light; the photon-excited dye generates an electric current in a separate, non-silicon-based semiconductor material (e.g., titanium dioxide, TiO_2). Chu explainedt that DSSC are less expensive than c-Si cells, but they also have a lower efficiency than both c-Si and TFPV cells (with a maximum reported efficiency of just over 11%) and suffer from some of the same stability problems that other[18] TFPV cells have.

   Following Chu's talk, Dr. Qingbo Meng of the Chinese Academy of Sciences, Beijing, China, noted that not only are DSSCs less expensive than c-Si cells, they are also easier to produce. In China, researchers are investigating whether lithium iodide (LiI), the traditional electrolyte material used in DSSCs, can be replaced by the less expensive aluminum iodide (AlI_3) to bring their cost down even further.

   Also following Chu's talk, Dr. Laurie Peter, University of Bath, UK, briefly described the history of DSSC technology, including Grätzel's discovery and then Massachusetts-based Konarka Technologies' commercialization of DSSC. Today, UK-based G24 Innovations (G24i) is selling another, proprietary DSSC technology. Meanwhile, scientists at the Fraunhofer Institute for Solar Energy Systems ISE, Germany, and elsewhere are continuing to investigate new ways to increase the efficiency of DSSC technology. As Peter explained, while the greatest reported solar energy conversion efficiency of a DSSC is 11.4%, that record is for a single cell in a research laboratory setting. Efficiencies in practical settings are lower, on the order of 8-9%.

2. *Conducting polymer solar cells*. Chu explained that, like DSSC, conducting polymer solar cells are potentially cheaper to manufacture than other types of PV technologies because they use semiconducting polymer materials instead of silicon, but they are not as efficient. They are also not very stable, with typical longevity for conducting polymer cells being only 3 to 5 years. Following Chu's presentation, Dr. Peter Bäuerle of Universität Ulm, Ulm, Germany, remarked that Konarka recently reported 6.4% efficiency, which is the highest performance to date for a conducting polymer solar cell in a research laboratory setting. However, the company's reported rooftop efficiency is only 3.3%. Dr. Zhigang Shuai, Tsinghua University, Beijing, China, commented on some of the research approaches being taken in an effort to increase the efficiency of polymer solar cells. These include using different types of polymers and nanostructured materials.

3. *Molecular (or "small molecule") organic cells.* As with the other new-concept technologies, molecular organic cells are potentially cheaper than silicon wafer and

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[18] While identified by Chu as a "new concept" technology, DSSC are also considered a type of TFPV.

thin-film technologies, both because of the materials used and because of their manufacturing processes. However, their solar energy conversion efficiency is only about 4%. As Bäuerle pointed out following Chu's presentation, Heliatek GmbH, Dresden, Germany, reported an efficiency of about 6%, which is the record for small molecule organic solar cells at the moment. Their limited efficiency is due in part to the fact that most currently available molecular semiconductor materials absorb only a narrow wavelength of light and therefore are not capable of harvesting much light.

Also following Chu's presentation, there was a question about indium tin oxide (ITO), one of the materials commonly used as an electrode in organic solar cells[19] and the movement to steer away from ITO because of sustainability issues (i.e., there isn't enough indium in the earth to provide for large-scale production). However, not all participants agreed that sustainability is an issue. In China, for example, the supply of ITO is not considered to be in short supply. Sustainability aside, there was still some concern expressed about the use of ITO because of performance and stability problems stemming from indium's chemical reactivity with organic materials in the cells.

The Search for Earth-Abundant Materials

Discussion around the resource implications of CdTe-based TFPV's potential expansion in the future led Dr. Laurie Peter, University of Bath, UK, to speculate on the availability of PV technology resources in general and whether the earth actually provides enough materials to realize the large-scale production of solar-generated electricity. He noted that both Cd and Te, for example, are quite rare in comparison to other elements in the earth's crust, like zinc (Zn), copper (Cu) and tin (Sn). Zn, Cu and Sn are also relatively cheap compared to some of the elements being considered for next-generation PV technologies, like indium (In). He asked: Is there a way to replace some of the more expensive, less abundant and potentially environmentally harmful materials that are currently being used with less expensive, more abundant, non-toxic materials? He argued that part of the reason that Te and many of the other materials being used today is historical and that chemists need to re-visit the periodic table of elements, as well as historic work, and experiment with new combinations of materials that would have the same properties as, for example, CIGS, but which would be more suitable for long-term, scaled-up use. To his knowledge, there are only a handful of research groups investigating the performance of alternative materials in PV cells.

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[19] The organic material is typically sandwiched between a layer of ITO and a layer of another electrode material.

The Future of PV Technologies

Chu emphasized four important next steps for advancing solar cell technologies:

(1) Improve existing processing technologies for first-generation c-Si solar cells. Even if the cost of silicon were to significantly drop, it would affect only 60% of the cost of a c-Si solar cell module. The processing and manufacturing of the materials and cells still need to be improved as well in order to bring the remaining 40% of the cost of c-Si technology down.
(2) Develop new materials for both thin-film and new-concept PV technologies, not just in order to bring the cost down but also for performance reasons.
(3) Continue to develop new structures, processes and concepts for both thin-film and new-concept PV technologies in order to improve the performance of these potentially less expensive technologies.
(4) Combine chemists' efforts with those of scientists in other disciplines (e.g., physics, materials science and engineering).

Chu's overview prompted several questions about which, if any, of the multitude of PV technologies currently being explored and developed is likely to be the most successful in terms of very large-scale delivery of electricity worldwide. For example, which of these technologies are more (or less) resource- or cost-limited and therefore less (or more) likely to be widely adopted? Chu responded that silicon is still the "best" material in terms of efficiency and that, within the next ten years or so, Si-based cells will become more affordable because they will be built with less Si than they are today. However, some of the other thin-film materials, like CiGS, will become more popular over time. He also predicts that molecular organic solar cells in particular will become very important in the future because of their low cost, although their efficiency and particularly their stability will need to be improved.

The fact that the efficiency and stability of molecular organic solar cells will need to be improved before they can become a viable option for large-scale use led into further discussion about the many basic scientific challenges that still remain. As Peter put it, "There is still a lot of chemistry that needs to be figured out."

Converting Solar Energy into Electricity

The widespread use of silicon-based photovoltaic (PV) cells, which convert solar energy directly into electricity, is limited by their high cost. What must be achieved before PV cells can become an affordable, sustainable mode of energy? During the final wrap-up session of CS3, a breakout group identified the following as one of the most pressing scientific challenges

Develop low-cost, non-toxic, earth-abundant PV materials for use in next-generation PV cells.

IV

STORING SOLAR ENERGY[20]

While finding ways to reduce the cost of water-splitting catalysts, increase the efficiency of biomass conversion, and build better-performing next-generation PV technologies will be vital to making solar energy-derived fuels competitive with fossil fuels, a couple of CS3 participants remarked that it is just as important that chemists figure out how to store all this energy once it has been converted. After all, as Dr. Daniel Nocera of the Massachusetts Institute of Technology, Cambridge, Mass., stated, "you can't run a society only if and when the sun shines." He argued that solar energy amounts to less than 0.1% of the energy market today not just because of cost and other material and manufacturing issues but also because of a lack of long-term stationary storage options.[21] Until solar energy can be stored for future (long-term) use, solar energy conversion technologies will have a difficult time penetrating the global energy market. The focus of the fourth session of CS3 was on solar energy storage technologies, with much of the discussion revolving around differences between personalized and centralized storage as well as on types of chemical fuels that should and could be stored. This chapter summarizes that discussion.

Ways to Store Solar Energy

Nocera opened the session with a brief overview of the various ways that solar energy can be stored:

(1) *Mechanically, through compressed air energy storage*. Solar energy can be used to compress air in underground reservoirs (e.g., aquifers, salt caverns) such that when the air is de-compressed, about 0.5 megajoules (MJ)/kg of energy are released.

(2) *Hydroelectric pumping systems*. Solar energy can be used to pump and store water in uphill reservoirs such that when the water flows back downhill, it releases about 0.001 MJ/kg energy. Nocera remarked that the energy density using this method is so low that hydroelectric pumping can't really be used for practical purposes.

(3) Batteries. Energy yield of batteries ranges from 0.54-0.72 MJ/kg for lithium (Li) batteries to 0.14-0.22 MJ/kg for nickel-cadmium (NiCd) batteries to 0.14-0.17 MJ/kg for lead (Pb) batteries. That's about as energy dense as batteries can be without making them

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[20] This section summarizes the highlights of the presentations and discussion that occurred during the fourth session of CS3, "Storage, Transportation, and Distribution of Discontinuously Supplied Energy," which was organized by Dr. Alvin Compaan of the University of Toledo, Toledo, Ohio.

[21] Storage is also a very important issue with respect to using converted solar energy for transportation purposes, an area of energy use that was mentioned but not elaborated on during CS3. Most of the discussion focused on stationary energy use.

any heavier than they already are. Nocera opined that, while batteries are good for transportation because their stored energy can be so quickly extracted, they are not a very good option for long-term, non-grid storage.

(4) Capacitors. While capacitors can store energy, their yield is only about 0.01 MJ/kg (supercapacitors) to 0.0206 MJ/kg (ultracapacitors).

(5) Chemical bonds: Chemical bonds have the highest energy density of any solar energy system. Compressed hydrogen gas (70 MPa H_2), for example, yields 143 MJ/kg, and other liquid fuels yield on the order of 44 MJ/kg. As Nocera explained, "nature 'chose' chemical fuels for storage" because of this high energy density and, moreover, "nature 'chose' to fix hydrogen with CO_2." He argued that perhaps we should take our cues from nature and not only use chemical bonds as our primary mode of long-term solar energy storage but also fix the hydrogen (i.e., the H_2 derived from water splitting) with CO_2 and make liquid fuels. However, as discussed in Chapter I, chemists have yet to develop a practical solar-powered way to reduce CO_2. Until that goal is reached, Nocera's vision of a personalized energy system relies on the use of H_2 as a fuel.

The Storage of Distributed Energy

Nocera remarked that, in addition to storage technologies being a key driving force of market penetration, personalized storage technologies in particular will also be key to making solar energy an accessible option for the non-legacy world – that is, the three billion people alive today that are considered low-energy users (e.g., people who use off-grid energy) plus an additional three billion low-energy users who will be inhabiting the planet over the next century. Most of the increased energy consumption worldwide over the next several decades will be among these six billion people. While the legacy world would arguably be better served by centralized grids, for example with converted solar energy being stored in batteries (see discussion below), the non-legacy world be better served by a decentralized system, with each housing complex or building relying on its own individual storage unit.

However, in order to make solar energy an accessible option for people who use off-grid energy, new types of solar energy storage systems need to be developed. The challenge is greater than simply scaling down currently existing systems. Nocera compared it to the challenge of designing personal computers: "You can't simply make mainframes smaller. You have to start from scratch and design new, personal computers. In much the same way, you can't simply scale down currently existing systems to meet the demands of all the new energy users. You need to create new personalized systems." As is the case with so many next-generation solar energy technologies, the question is, how?

Nocera described his vision of a personalized energy system, which is based partly on work that his laboratory group has done with a new water-splitting catalyst (see Chapter I for a more detailed discussion of the chemistry of the catalyst): A rooftop PV array would convert solar energy into electricity for use during the day, with surplus electrical energy being diverted into a water-splitting device for the production of H_2 and O_2. The H_2 and O_2 would be stored in a local tank and, at night, recombined in a fuel cell[22] to generate whatever electricity is needed to power the home when the PV array isn't operating. In theory, powering a single home or cluster of dwellings would require only a very small amount of water as raw material. As mentioned in Chapter I, Nocera and has entered into an agreement with Sharp Electronics to integrate the water splitting part of the system with Sharp's PV technology. Nocera emphasized that his work is not necessarily "the answer," rather it is the beginning of a new area of research and development in decentralized solar energy storage.

What Kind of Chemical Fuel?

Following Nocera's presentation and re-visiting some of the discussion that took place during the first session (as summarized in Chapter I), Dr. Robert Schlögl of Fritz-Haber-Institute der Max-Planck-Gesellschaft, Berlin, Germany, stated that while, in the past, hydrogen fuel was viewed as the only option for the chemical storage of solar energy, scientists have since realized that in fact there are other options and other types of fuels. He remarked that different types of fuels could be produced depending on the situation. Dr. Etsuko Fujita, Brookhaven National Laboratory, Upton, New York, commented on the desirability of methanol, because it can be used either as a stationary or transportation fuel and because there are many options available for its production. Either way -- whether H_2 (e.g., H_2 produced from water splitting) is used as a fuel by itself or converted into another fuel -- H_2 will likely become a very important component of the future energy systems of many countries. Therefore, Schlögl said, we need to start thinking about how to store it. He re-emphasized, however, that although chemists have successfully demonstrated that it is possible to use solar energy to power the various chemical reactions that comprise water splitting, none of these processes have been advanced to a point where they can be applied. Chemists have yet to develop artificial photosynthesis catalysts that not only work efficiently enough to apply in power station or other energy conversion systems but also are made of abundant, affordable materials

Nocera then asked whether it would be possible to scale down the CO_2 reduction process so that it could be used in personalized energy storage systems. That is, are there catalysts that could be used to reduce CO_2 and form other fuels besides hydrogen for use in small energy systems? Schlögl responded that, yes, it is possible, but it would require the development of new reactors and simpler processes. In other words, while the chemistry of catalysis is obviously a tremendously important issue for many areas of solar energy science and technology, in this case there are other issues of concern. Dr. Sossina Haile, California Institute of Technology, Pasadena, California, noted that scientists at Pacific Northwest National Laboratory are developing miniaturized energy-converting technologies that might be applicable to this sort of small-scale CO_2 reduction scenario.

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[22] A fuel cell is a device that converts chemical energy into electrical energy. The simplest fuel cells use H_2 as their energy source, reacting the H_2 with O_2 to produce water and, in so doing, release energy. Other fuel cells use various hydrocarbons, like methane, as their chemical source, converting the methane to hydrogen first and then reacting the hydrogen with oxygen to release energy.

Large-Scale, Grid-Connected Solar Energy Storage

During the discussion following Nocera's presentation, Dr. Ferdi Schüth, Max-Planck-Institut für Kohlenforschung Kaiser-Wilhelm-Platz, Mülheim, Germany, reiterated the need to consider different types of storage systems for different locations, depending on local infrastructure and need. While it might make sense to store solar energy as a gas or liquid chemical fuel (e.g., hydrogen, methanol or methane) in areas without grid infrastructures, it makes better sense to "stay electric" as long as possible in grid-connected areas. Building a centralized energy system around solar-powered electricity, however, will still require buffering (i.e., storage capacity). Germany, for example, is required to maintain a 90-day supply of oil reserves, which corresponds to about 20 million tons. Moving away from oil would require finding an alternative way to store 90-days worth of fuel.

Dr. Jürgen Janek, Justus Liebig University Giessen, Germany, commented on the feasibility of using batteries as one of those alternatives. He remarked that unlike most of the other technologies discussed during the course of the symposium, there is the (electro)chemical challenge plus the challenge of coordination of a battery-based storage grid. A grid-connected battery storage system of that size need only be designed and organized correctly. Other than these brief comments, the scientific and technological challenges of advancing battery storage were not addressed in any detail.

Finally, Haile described a centralized solar energy storage energy vision for the future that involves an approach analogous to what Nocera laid out for personal use: In addition to producing electricity for daytime use, centralized plants would also use some of the solar energy captured during the day to produce fuel via a ceria-based thermochemical process and the fuel used to deliver electricity at night. She and her research team have demonstrated that ceria can be used as a thermochemical reaction medium for the production of hydrogen, syngas[23] or methane upon exposure to water and CO_2. Based on the amount of ceria currently available (about 40 megatons worldwide, which is relatively abundant compared to other elements), one could conceivably build 50,000 such 100-megawatt power plants at the equivalent of about US$140k each (in raw ceria materials cost).

Storing Newly Harnessed and Converted Solar Energy

Chemists must develop systems that not only convert solar fuel into other forms of energy but also store that converted energy for future use. This is an especially critical issue for areas of the world without access to centralized energy delivery systems. What must be achieved in order to build low-cost, sustainable solar storage systems? During the final wrap-up session of CS3, a breakout group identified the following as the most pressing scientific challenge:

Develop new catalysts and materials from low-cost, earth-abundant elements that can be used to build affordable, sustainable solar energy transformation-and-storage systems.

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[23] Syngas is a combustible gas mixture that contains carbon monoxide and hydrogen – it can be used as a fuel or as an intermediate in other types of fuel production systems.

APPENDIX A

Program

First Chemical Sciences and Society Symposium (CS3)
Kloster Seeon, Germany, July 23-25, 2009

Powering the World with Sunlight

Wednesday, July 22, 2009

Afternoon	Arrival and registration
6:00 PM	Welcome and informal dinner

Thursday, July 23, 2009

7:30 AM	Breakfast
8:45-9:00 AM	Welcome and Opening by Klaus Müllen, GDCh President
Session 1	***Artificial Photosynthesis, Photocatalytic Water Splitting, and CO_2 Fixation***, organized by Dr. Hauro Inoue, Tokyo Metropolitan University, Tokyo, Japan
9:00-9:40 AM	Introductory Lecture by Dr. Kazunari Domen, University of Tokyo, Japan
9:40-10:30 AM	Statements and Discussion
10:30-11:00 AM	Break
11:00-12:00 PM	Statements and Discussion, cont.
12:30-2:00 PM	Lunch
Session 2	***Solar Radiation to Energy via Biomass***, organized by Dr. Laurie Peter, University of Bath, UK
2:00-2:40 PM	Introductory Lecture by Dr. James Barber, Imperial College London, UK
2:40-3:30 PM	Statements and Discussion
3:30-4:00 PM	Break
4:00-5:00 PM	Statements and Discussion, cont.

Friday, July 24, 2009

7:30 AM	Breakfast
Session 3	***Photovoltaics: Organic Solar Cells, Inorganic Solar Cells, and Dye-Sensitized Solar Cells***, organized by Dr. Chen-Ho Tung, Chinese Academy of Sciences, Beijing, P.R. China
9:00-9:40 AM	Introductory Lecture by Dr. Junhao Chu, Shanghai Institute of Technical Physics, Shanghai, P.R. China
9:40-10:30 AM	Statements and Discussion
10:30-11:00 AM	Break
11:00-12:00 PM	Statements and Discussion, cont.
12:30-2 PM	Lunch
Session 4	***Storage, Transportation, and the Distribution of Discontinuously Supplied Energy***, organized by Dr. Alvin Compaan, University of Toledo, Toledo, Ohio, U.S.A.
2:00-2:40 PM	Introductory Lecture by Dr. Daniel G. Nocera, Massachusetts Institute of Technology, Cambridge, Mass.
2:40-3:30 PM	Statements and Discussion
3:30-4:00 PM	Break
4:00-5:00 PM	Statements and Discussion, cont.
6:00-7:30 PM	Dinner

Saturday, July 25, 2009

7:30 AM	Breakfast
9:00-10:30 AM	***Breakout Sessions***, organized by Dr. Ferdi Schüth, Max-Planck-Institut für Kohlenforschung Kaiser-Wilhelm-Platz, Mülheim, Germany.
10:30-11:00 AM	Break
11:00-12:00 PM	***Wrap-Up and Recommendations***

APPENDIX B

List of Participants

China

Prof. Dr. Chen-Ho Tung, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing: *CS3 Scientific Committee member*
Prof. Dr. Junhao Chu, Shanghai Institute of Technical Physics, Shanghai
Prof. Dr. Fang Huang, Research Center for Photosynthesis, Institute of Botany, Chinese Academy of Sciences, Beijing
Prof. Dr. Can Li, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian
Prof. Dr. Qingbo Meng, Institute of Physics, Chinese Academy of Sciences, Beijing
Prof. Dr. Zhigang Shuai, Department of Chemistry, Tsinghua University, Beijing: *Chinese Chemical Society [CCS] and National Science Foundation of China [NSFC] liaison*

Germany

Prof. Dr. Ferdi Schüth, Max-Planck-Institut für Kohlenforschung Kaiser-Wilhelm-Platz, Mülheim: *CS3 Scientific Committee member*
Prof. Dr. Peter Bäuerle, Universität Ulm, Abteilung Organische Chemie II, Ulm
Prof. Dr. Jürgen Janek, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Gießen
Prof. Dr. Walter Leitner, Institut für Technische und Makromolekulare Chemie, Aachen
Prof. Dr. Dr. h. c. Hartmut Michel, Max-Planck-Institute für Biophysik, Abteilung Molekulare Membranbiologie, Frankfurt am Main
Prof. Dr. Klaus Müllen, Max-Planck-Institut für Polymerforschung, Mainz
Prof. Dr. Robert Schlögl, Fritz-Haber-Institute der Max-Planck-Gesellschaft, Berlin
Dr. Kurt Begitt, Gesellschaft Deutscher Chemiker e.V. (GDCh), Frankfurt am Main: *GDCh liaison*
Dr. Markus Behnke, Deutsche Forschungsgemeinschaft (DFG), Bonn: *DFG liaison*

Japan

Prof. Dr. Haruo Inoue, Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Tokyo: *CS3 Scientific Committee member*
Prof. Dr. Kazunari Domen, Department of Chemical System Engineering, School of Engineering, University of Tokyo, Tokyo
Prof. Dr. Michikazu Hara, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama
Prof. Dr. Kazuhito Hashimoto, Department Applied Chemistry, School of Engineering, The University of Tokyo, Tokyo
Prof. Dr. Osamu Ishitani, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, Tokyo
Prof. Dr. Koji Tanaka, Institute for Molecular Science, Okazaki
Dr. Teruto Ohta, The Chemical Society of Japan (CSJ), Executive Director, Secretary

General, Tokyo: *CSJ liaison*
Prof. Dr. Yoshio Okahata, Senior Program Officer, Chemistry Group, Research Group for Science Systems, Japan Society for the Promotion of Science (JSPS) and Professor, Graduate School of Bioscience and Biotechnology, Tokyo Institute of Technology: *JSPS liaison*

United Kingdom

Prof. Dr. Laurie Peter, Department of Chemistry, University of Bath, Bath: *CS3 Scientific Committee member*
Prof. Dr. James Barber, Imperial College London, London
Prof. Dr. Anthony Harriman, Professor of Physical Chemistry and Co-Director of the Molecular Photonics Laboratory, Newcastle University, Newcastle upon Tyne
Prof. Dr. Timothy Jones, Department of Chemistry, University of Warwick, Coventry
Prof. Dr. Andrew Mills, Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow
Prof. Dr. Chris Pickett, School of Chemical Sciences & Pharmacy, University of East Anglia, Norwich
Dr. Richard Pike, Chief Executive, Royal Society of Chemistry (RSC), London: *RSC liaison*
Katie Daniel, Senior Portfolio Manager, Engineering & Physical Sciences Research Council, Swindon: *EPSRC liaison*

United States

Prof. Dr. Alvin Compaan, Department of Physics and Astronomy, University of Toledo, Toledo, Ohio: *CS3 Scientific Committee member*
Dr. Mark Davis, Principal Scientist & Group Manager of Chemical and Catalyst Sciences, National Renewable Energy Laboratory, Golden, Colorado
Dr. Etsuko Fujita, Senior Chemist, Chemistry Department, Brookhaven National Laboratory, Upton, New York
Prof. Dr. Sossina M. Haile, Materials Science and Chemical Engineering, California Institute of Technology, Pasadena, California
Prof. Dr. Stephen Maldonado, Department of Chemistry, University of Michigan, Ann Arbor, Michigan
Prof. Dr. Daniel G. Nocera, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts
Prof. Dr. Mary Jane Shultz, Department of Chemistry, Tufts University, Medford, Massachusetts
Dr. Julie Callahan, Global Network Content Development Manager, American Chemical Society (ACS), Washington, D.C.: *ACS liaison*
Dr. Carol A. Bessel, Program Director, Inorganic, Bioinorganic, and Organometallic Chemistry Program, National Science Foundation (NSF), Arlington, Virginia: *NFS liaison*
Dr. Luis Echegoyen, Director, Division of Chemistry, National Science Foundation, Arlington, Virginia: *NFS liaison*

Other Participants

Dr. Leslie A. Pray, Science Writer, Holyoke, Massachusetts, United States
Sarah Everts, European Correspondent, *Chemical & Engineering News*, Berlin, Germany