Materials Issues in a Hydrogen Economy

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Editors

Puru Jena
Virginia Commonwealth University

Anil Kandalam
McNeese State University

Qiang Sun
Peking University

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PANEL SUMMARY

SCOTT W. JORGENSEN

Chemical and Environmental Sciences Lab, GM Research and Development, 30500 Mound Rd, Warren, MI 48090, USA

R. CHAHINE

Hydrogen Research Institute, Universite Du Quebec a Trios-Riviers, 3351 Des Forges Bldg, Trios-Riviers, Quebec G9A 5H7, Canada

J. P. MEYERS

Materials Science and Engineering, The University of Texas at Austin, 1 University Station, Austin, Texas 78712, USA

G. D. PARKS

Research and Development, ConocoPhilips, 344A PL BTC, Bartlesville, OK 74004, USA

A. A. PUNDT

Universitat Gottingen, Friedrich-Hund-Platz 1, 37077 Gottingen, Germany

Y. FILINCHUK

European Synchrotron Radiation Facility, Swiss-Norwegian Bea Lines, 6 Rue Jules Horowitz, 38043 Grenoble, France

The main focus of this symposium, materials advances in the areas of hydrogen production, storage and fuel cells, reflects the world wide research focus on these key areas required to form the technical foundation for a hydrogen economy. The sessions on tank engineering materials, safety, education and standards also reflects the growing emphasis on these issues which will become the focus once the initial technical hurdles in science and or engineering are surmounted. Better materials are very much needed in each of these areas either to improve performance, and durability or decrease costs. The conference summarized the progress made to date in these field and highlighted the progress that remains to made to make hydrogen a dominant energy carrier in all aspects of the world economy. This review follows the flow of hydrogen through a constructed hydrogen economy to summarise the papers and discussion at the ISHE, referencing the barriers and progress globally.

Because, like electricity, hydrogen is a secondary power source that must be generated from primary sources such as fossil fuels, nuclear energy, tidal energy, geothermal heat, solar energy or its' derivatives wind and biomass, the hydrogen economy necessarily starts with hydrogen production and possibly subsequent transportation to users. A few interesting papers were given showing advances in hydrogen production from solar energy either directly by photochemical or indirectly via photobiological processes. This is in line with the plenary talk that stressed the fact that "solar is the only energy source with sufficient capacity to fulfill the energy needs of the future" and urging that "we should be developing H_2 [technologies] not only for cars but for the big picture". In general, the progress described was more evolutionary than revolutionary perhaps due to the maturity of the energy supply industry, but these works describe significant progress on several fronts related to hydrogen production.

Production and Delivery

In the short term economics and existing infrastructure dictates that bulk hydrogen production will largely originate from fossil fuels. Production of hydrogen using an improved water-gas shift catalyst was described. In these experiments and calculations showed that subsurface copper promoted platinum activity and made the catalysts less susceptible to poisons. Other research focuses on the use of oxygen-permeable membranes in partial oxidation (POX) reactors. Results with planar membranes showed reasonable oxygen fluxes and high CO and hydrogen selectivities. Additional research on oxygen transport membranes is aimed at improving steam reforming of methane.

Electrolysis, like SMR, could serve for distributed or large scale production. Nano-composite electrodes for natural gas-assisted steam electrolysis were described, aimed at improving electrode activity and stability.

One advantage a secondary power source has is that it may be able to access energy in waste streams. Although hydrogen production form the reaction of water with aluminum has been studied extensively for decades, recently researchers have increased efficiency by using the reaction to produce high pressure hydrogen. Combined with the use of waste aluminum as a feedstock, this process is somewhat more economical and efficient than similar processes. In reference to the hydrogen economy this is not a global solution for hydrogen supply, but does illustrate the general concept of extraction of energy that would otherwise be lost in waste, a principle that may play a role in the larger suite of hydrogen generation techniques.

In contrast, photoelectrochemical hydrogen could be exercised on a large scale if the difficulties in cost effective production with appropriate land and water use were solved. Researchers from multiple locations discussed hydrogen production using direct photoelectrochemical water splitting. While none of the photocatalytic materials are near commercialization, progress is being made on efficiency and corrosion control. One technique discussed uses mesoporous transition metal oxides for photocatalytic hydrogen production, but most required ultraviolet light to affect water splitting. An approach less dependent on new materials is the use of concentrated sunlight to thermally decompose water. Here, the use of catalyst-coated monolith reactors to facilitate decomposition and "trap" oxygen formed was described. By cycling multiple systems using solar heat to release oxygen and prepare for continued hydrogen production a continuous hydrogen stream is possible. Other thermochemical cycles to facilitate thermal water splitting include the modified sulfur-ammonia cycle, and the sulfur-iodine cycle - the later used either directly or with use of oxygen transport membranes to improve hydrogen production. Of course an alternative approach is to use sunlight to power biological hydrogen production. Work with green algae seeks to increase the H_2 yields, optimize adsorption of sunlight, and explore cost-effective reactor designs.

Only one presentation dealt with hydrogen delivery- a review of challenges and recent developments in the field that have been funded by the US DOE. While possibly less glamorous, delivery either by pipeline or vehicle, or alternately delivery of another energy source with subsequent on-site hydrogen-generation is a key link in the hydrogen economy and must be properly developed.

Storage

Once created and delivered, hydrogen will frequently need to be stored. This is a requirement for use in vehicles. Many feel that improvement in this area is a major barrier to launching the hydrogen economy, though several auto makers have fielded vehicles using existing storage technology and some have demonstrated 300 mile range is possible for vehicles that represent a portion of world fleet. Nonetheless, greater storage capacity and lower cost would surely facilitate faster and deeper penetration into this key sector of energy use.

An accordingly large share, (more than 50%) of the oral presentations at the symposium, were dedicated to hydrogen storage. There was a profusion of screening and modeling results showing good synergy with experiments in the solid hydrides. As with the global research to date, the focus was largely directed toward high wt% or specific mass of storage techniques while less attention was given to volumetric density which can be an equally critical factor for onboard storage in some applications.

An increasing number of one-component systems, like $LiBH_4$ and $Ca(BH_4)_2$ have been shown to be in principle reversible, although at high temperature (~600°C) and hydrogen pressure (~200 bar). There were few such presentations at the ISHE, and this follows the trend of a continued but decreasing activity in the relatively mature field of known, simple, materials.

By contrast, a new trend in research on hydrogen storage systems is to modify and combine known light hydrides in order to improve their hydrogen storage properties; and several papers on this topic were presented. New developments center on doping existing compounds (introducing chemical substitutions) and making them react with other H-rich solids. These attempts to modify properties often bring very interesting results. Properly chosen a mixture of two hydrides desorbs hydrogen at lower temperature than a one-component system, sometimes accompanied by lesser amounts of biproducts, e.g. diborane or ammonia, in the desorbed hydrogen gas. The following systems were presented at the symposium:

- Borohydrides ($LiBH_4$, $Ca(BH_4)_2$) + binary hydrides (LiH, MgH_2);
- Borohydrides ($LiBH_4$, $NaBH_4$) + amides ($LiNH_2$, $NaNH_2$);
- Aminoborane (NH_3BH_3) + binary hydrides (LiH, NaH, CaH_2);
- Borohydride ($NaBH_4$) + alanate ($NaAlH_4$).

In some cases, the initial compounds form hydrogen-rich intermediate phases, which release hydrogen at lower temperature than the starting compounds. A number of such new phases were presented both by oral presentations and posters. These presentations were a mix of pure and applied research.

From the perspective of laying a foundation for a hydrogen economy, an experimental study of a two-component system might ideally provide information about the reactivity of the components, hydrogen desorption temperature and H-capacity. In addition the research should isolate the presence of new intermediate phases that may contain meaningful amounts of hydrogen, and thus may be used for H-storage on their own, and describe the existence of new decomposition products, which may reabsorb hydrogen. This data should be also supported by the thermodynamic information, showing that the reaction enthalpies are not excessively high. In general such a complete study is of greater scope than any one researcher's area of interest, or perhaps that of their funding body. Fortunately, when several works from around the world are taken together, as may be seen in major conferences, this complete picture begins to emerge.

In the ISHE it was possible to connect PCT diagrams which characterize the bulk properties of a system, with diffraction studies that help to determine which phases are involved in reactions when more than two components are present in the mixture. The measurement of PCT diagrams tends to go first, as they demonstrate whether the "destabilization" is achieved. Diffraction study can clarify the mechanism of such "destabilization", i.e. the reaction mechanism. In particular, the dehydrogenation process has to be analyzed for new intermediate phases, and for new hydrogen-poor (or hydrogen-free) decomposition products. The latter may be tested as starting compounds in rehydrogenation processes. New compounds may show different properties and maybe even reversibility!

Even if only two starting components are used, a system becomes complicated (multi-component) when hydrogen desorption begins. As a number of intermediate and decomposition products are involved, the system becomes multi-component, and thus it appears essential to know which components are involved in the crucial steps of hydrogen release. In several works an *in-situ* diffraction study of hydride mixtures was important in the identification of new phases and gives a sequence of intermediate compounds.

Thus, there were several reports searching not only for new H-rich substances, but also for new hydrogen-poor, relatively unstable phases composed of light elements, which may appear for the first time as decomposition products, but later may turn out to store hydrogen reversibly. Different catalysts can be tested at this stage. Finally, the properties of the system can be improved, for example by using nanoengineering.

The new accomplishments using the "hydrogenography" approach were presented in the study of solid solution and two phase metal. It would be interesting to see this or other very high throughput methods used in the light hydride systems. Thin films of multiple light hydrides can be deposited at various concentrations and studied by diffraction. A crystalline powder, as the most common form of hydrogen storage materials, can be studied by *in-situ* powder diffraction, both at variable temperature and hydrogen pressure. Such scan reveals all possible transformations of the new material or a continuum of mixtures aiming to destabilize the hydride. Such measurements can now be routinely done at some synchrotron beam lines and neutron facilities and upgrading them to support combinatorial work could hasten the discovery process. Inelastic and quasi-elastic studies of silicon and boron-containing hydrides show the power of these techniques.

Probing dynamics by experimental techniques, inelastic X-ray scattering, infra-red and Raman (vibrational) spectroscopies and NMR is also effective and instructive. These methods provided a link between structure and properties, providing fundamental information that helps to reduce the "gap" between theory and experiment. Dynamics is something hidden from routine crystallographic studies, which often represent structures as "static". The presentation on the dynamics of amino borane illustrated the knowledge that can be gained pairing theory and spectroscopy. Theoreticians, on the other side, will have difficulties modeling a system that is ill-defined. Given the lack of information about dynamics, many calculations aim to reproduce the structure only. Experimental information on structure dynamics provides reference points for density functional theory (DFT) calculations, thus helping to avoid the most common pitfalls of structure prediction. It was also shown how complete intermediate information is required to properly calculate reaction enthalpies and predict reversibility at pressures and temperatures acceptable for use in the hydrogen economy.

There was discussion on several occasions on the "gap of realities" between theory and experiments. One point raised in this connection was the value of a theoretician directly participating with experimental groups. This will help to apply theory directly and continuously to experimental activities, with immediate feedback in both directions. Theory often brings attention to subtle but important features, which experimentalists may not naturally notice, or even cannot directly measure. Likewise without rapid data to test predictions, theorists can only slowly refine models and may spend considerable effort on predictions made with incomplete models that yield less accurate predictions. This synergy seems to be growing world wide and will surely benefit all research in the area of hydrogen storage.

For the last 5 years research on metal-organic frameworks has shown considerable progress; most recently culminating in a series of materials storing 7 to 7.5 wt% excess hydrogen storage at 77K reviewed here. This work includes a MOF with 32 g per liter volumetric storage capacity and hope of exceeding 40g/L. The enthalpy of hydrogenation tends to be low in these materials so they fill rapidly; for example new data showing that MOF-74 initially exhibits an 8.8 kJ/mol adsorption enthalpy, which drops to half that value with 2 wt% hydrogen uptake, was discussed. Possible applications of these materials will be more likely if research can produce higher volumetric capacity and higher absorption enthalpy.

Spectroscopic techniques nicely compliment synthesis and capacity work. One paper reviewed recent work on neutron powder diffraction, where MOFs loaded with different deuterium pressure were studied to directly pin point the location of hydrogen in these porous systems. For the first time the absorbed hydrogen molecules were located in the organic linker, and this highlights their importance. It would be interesting to test this approach on the other systems that store weakly bound hydrogen.

There was also an interesting triangle of presentations on Metal-H_2 (dihydrogen) complexes. One was a reaffirmation of the theory of multiple (up to 6 molecule binding) of hydrogen in metal assisted organics (so called soft chemisorption, e.g. C_2H_4-Ti); a second was announcement of the synthesis on the titanium complex at the picogram scale (hopefully soon to be independently confirmed); and thirdly a review on metal-H_2 complexes by the original discoverer, which showed that of the more than 600 compounds found so far only ~ 2 % contain 2 hydrogen molecules and the remaining only one molecule of hydrogen. It also mentioned the difficulties in obtaining high capacity materials in the condensed phase. These three papers together, point to the previously mentioned gap between prediction and successful creation of materials. Extensive theoretical predictions suggest each Sc atom in a $Sc_{12}C_{60}$ cluster may take 4 hydrogen molecules reaching 7 wt% of hydrogen storage capacity, but the clustering of these Sc atoms may affect material stability. The hydrogen absorption enthalpy for $Li_{12}C_{60}$ is predicted to be 6.4 kJ/mol based on a baseline structure. However, recent experimental results show completely different metal-fullerene structures displaying 0.2-0.5 wt% uptake of H_2 at 77K. At present it is unclear if the predictive models need refinement or if new synthesis techniques are required. It is clear that close interaction between experiment and theory groups is needed to resolve the situation.

On balance significant progress made to date over a very short time both reflects and validates the level of effort, the creative and deductive thought, and the amount of funding directed at hydrogen storage. Such funding must be sustained to drive this technology to a point where it is widely applicable in the hydrogen economy.

Fuel Cells

The final step in the hydrogen flow through a hydrogen based economy is consumption for useful work. While internal combustion engine technology has been known for some time, the major research effort is on fuel cells. Fuel cells also date to the 19th century, but application has only been likely with recent improvements in power density. While increasingly sophisticated stationary and mobile fuel cells have been fielded over the last 10 years, durability and cost have inhibited wide scale production in mobile applications.

During the ISHE, good progress toward the various international targets was reported. Durability of the new membranes can provide 40 to 50x reduction in fluoride evolution and last as much as 20x longer than their predecessors. New R&D efforts are aiming to increase the operation temperature and humidity requirements in order to reduce the cooling requirements and simplify the BOP.

Progress was also reported in modeling the reaction and transportation processes on fuel cell catalysts and through membranes, using multiple paradigms as well as starting from first principle quantum mechanics to 'train' a reactive force field that can be applied for large scale molecular dynamics simulations. It is expected that the model would "enable the conception, synthesis, fabrication, characterization, and development of advanced materials and structures for fuel cells".

Education and Safety

As illustrated by some of the latter papers, there is a role for governments around the world in educating the public and facilitating the transition. In addition, it will eventually be highly important to understand hydrogen embrittlement of metals, and the compatibility of materials in a moderate to high pressure hydrogen environment. Depending on the storage mode, this material may need to tolerate cryogenic temperatures or elevated temperatures. Work in these areas is not as intense as those discussed above, but as the hydrogen economy nears and applications increase, it may be expected that structural materials, standards, and education issues will grow in both public awareness and concomitantly in technical importance.

Hydrogen Economy beyond the Transportation Sector

Finally, as in every hydrogen conference, there was discussion of the issue of the DOE Hydrogen storage targets for onboard vehicle and the oft encountered comments of "being difficult to achieve". In all fairness these targets started as

being US targets but similar targets were adopted years later by other national and international H_2 programs. Are they too high? We have to achieve high targets if we are seeking a world wide market application of FCVs, not only for personal mobility but for the transport of goods and other uses. By many accounts, mass production of FCVs will not happen before many years. By 2025, according to the recent report of the Air Resources Board of the state of California which has in the past set a tone for America and the rest of the world when it comes to pollution. So the questions arose, is an FCV the only hydrogen application out there, and given that several hydrogen technologies suffer from slow kinetics, how do we accelerate it? The answer is an application in demand where the targets are easier to hit. For example, cordless electric applications ranging from laptop computers to power tools where there is a real demand for longer run times. These applications are mostly going to lithium ion batteries. The Li battery market is estimated at $5 billion/year with double digit annual increase. So Instead of directing the quasi-totality of the R&D efforts on developing storage materials for the ultimate FCV application, which require that we meet a set of technical targets that is difficult to achieve, some felt we should invest efforts on these other applications where the targets are easier to hit than the corresponding DOE hydrogen targets. Battery targets are often an order of magnitude lower than H_2 storage targets, for example $900-1500/kWh compared to $2-8/kWh of storage and similar differences in life and energy density. Even accounting for the fuel cell mass and cost these are still a morel likely entry point. This might be where the hydrogen moves from a chemical industry technology to a wider field of application. The availability of such a system will create a real market and the crucially important supply chain where technological progress and innovations happen most rapidly on the trip up the experience curve. A strong consumer demand and rapid market 'kinetics' coupled with aggressive R&D could then open an automotive fuel cell / hydrogen-storage market. With the huge talent within the hydrogen scientific community there is reason to feel a hydrogen economy is possible.