HYDROGEN STORAGE RESEARCH ACTIVITIES AT OAK RIDGE NATIONAL LABORATORY

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Abstract

Today our world needs assurance of an adequate supply of many commodities, one of the most important of which is energy. The *Rerum Novarum* postulate states, “In our time, in particular, there exists a form of ownership more important than land: the possession of know-how, technology, and skill.” Knowledge and technology in action, working synergistically to improve survival and standard of living of unprecedented multitudes, are enabling solutions to supply the world’s energy needs. The expanded use of hydrogen as an energy source will help ensure a safer, higher standard of living for the world’s peoples. The objective of this symposium is to advance the knowledge, technology, and skill necessary for the use of hydrogen as an energy source.

The principal, technical issue of developing a hydrogen economy is hydrogen storage. In this presentation, hydrogen storage issues are addressed, and hydrogen storage research being conducted at Oak Ridge National Laboratory (ORNL) is described. A particular concern is finding a method of vehicle storage of hydrogen that offers low weight, low volume, high levels of safety, and fast refueling. Addressing this challenge is a high priority at ORNL and a major goal of the U.S. national laboratories.

Preamble

Mr. Chairman, scientists and engineers, ladies and gentlemen, good morning. It is indeed my pleasure to address this distinguished group of engineers, scientists, and technologists who have gathered for the pursuit of knowledge concerning hydrogen technology. I know you labor year-round to make a difference—to improve and increase the global use of safe and beneficial sources of energy. I join you in this task, made even more important by these troubled times. At the outset, I want you to know that I am expressing my individual views, unless I state otherwise. Also, I will quote freely from a person whom I greatly admire, U.S. Nuclear Regulatory Chairman Nils J. Diaz [1].

The Procession of Knowledge and Technology

Today, our great world needs to have assurance of supply of many commodities, one of the most important of which is energy. In this respect, I would like to begin with a quote:

> In our time, in particular, there exists another form of ownership which is becoming more important than land: the possession of know-how, technology, and skill. The wealth of a nation is based much more on this kind of ownership than on natural resources.

I am sure you would not be surprised if I were to attribute this far-reaching statement to a year 2003 philosopher, economist, or entrepreneur. However, the statement is much older. It is a quote from the Encylic *Rerum Novarum*, published in 1891 [2]. As pertinent as it was in 1891, it is even more relevant today, when a microchip can be worth much more than gold; when services are more important than the production of goods for an economy; when disease is being conquered by mapping the human genome; and when virtual reality is no longer a dream, but a useful tool.

The impressive scientific and technological achievements of the last century could not have been envisioned in 1891, yet they have irrefutably confirmed the far-reaching conclusion of that visionary document. There is no doubt that the world has been shaped by the sociopolitical revolutions of the last 300 years—the American, the French, and the Bolshevik Revolutions—and by events in our recent sociopolitical world. But it has also been shaped by the scientific and technological revolutions that have spanned the twentieth century, in the midst of great wars and massive economical developments.

As extraordinary as all these twentieth century developments have been, all is not well. I will first quote and then comment upon a few thoughts by George Gilder [3], who wrote regarding the early twentieth century:

> It was the survival of unprecedented multitudes of human beings at ever increasing standards of living, together with a new intolerance toward the persistence of conditions of poverty that had previously been accepted as inevitable.

That is, at the beginning of the twentieth century, it was believed that there would always be poor peoples. Today, all peoples strive to be rich. I believe that Gilder stated what is a key and real crisis of the twentieth and twenty-first centuries. In many ways, his succinct yet poignant statement expresses a fundamental social, political, and economical issue confronting mankind. It describes a root cause of many of today's great problems, and it has to be addressed with urgency and with solutions.

The rising expectations of humanity depend largely on reliable, abundant, inexpensive energy supply. It is obvious to me that real solutions to this global energy supply problem can be found in democratic systems of government, where there is pursuit of happiness and free enterprise. Indeed, I believe that solutions are found in the exercise of the *Rerum Novarum* postulate: "the possession of know-how, technology, and skill." In other words, education and technology in action, working synergistically to improve the survival and the standard of living of unprecedented multitudes, are enabling solutions.

Knowledge has a continuing and accelerating influence in mankind's progress, and specifically so in the increasing worth of technology. Wealth, as measured by physical resources, is declining while the value of technological capabilities and innovation is increasing. For many nations, technological know-how and pressing societal needs ameliorated the many "crisises" we have encountered, such as the population (food supply) crisis, the energy crisis, the nuclear winter crisis, and the environmental pollution crisis. From a modest, in present terms, industrial revolution, the more developed nations accelerated into the automobile era, the airplane age, the nuclear age, the space age, the era of information technology, and now the biogenetics era. In so many ways, key scientific discoveries are essential components of this period of mankind. It is the better understanding and use of the physical world and associated applications that have made possible or lead to the understanding and progress in other sciences and are therefore a major contributor to mankind's progress. For example, evolution was once a very controversial theory; it is now a tool, a process to improve our world, to fight disease, to grow crops, and to feed people.

Knowledge makes possible what is needed to achieve productivity and improve the quality of life in many areas. But knowledge alone cannot succeed without usable energy. Without abundant, reliable, inexpensive, safe energy, there would be little of what we enjoy today. We would be much poorer. Energy, well distributed and affordable, is one of the indispensable and enabling components of the know-how era.

The device that consumes most of the world's energy is the personal vehicle, or automobile. For example, automobiles consume ~27% [4] of the total energy in the United States. Therefore, the remainder of this talk will focus on hydrogen storage in automobiles.

Hydrogen Storage Issues [5]

Hydrogen storage is the critical enabling technology that must be developed for the widespread use of vehicles powered by either hydrogen-burning internal combustion engines or fuel cells. Hydrogen-based fuel cells and internal combustion engine technology, and hydrogen production methods, are much more mature than are the technologies for storage of hydrogen. Storage is the major challenge for the hydrogen economy. After all, the internal combustion engines of Boris Sheliskh, in besieged Leningrad, operated with hydrogen more than 60 years ago. Yet, the methods of hydrogen storage have changed little since then.

Hydrogen storage challenges arise primarily from its low volumetric density: Hydrogen requires several times more storage space than any other fuel for a comparable amount of energy. For decades, hydrogen has been stored as a compressed gas and as a cryogenic liquid. It is used extensively in industry and as a spacecraft fuel. However, its use to power personal vehicles presents unique challenges that existing storage systems do not answer:

- Sufficient hydrogen must be stored aboard the vehicle to propel it for several hundred miles, in a system that can be quickly and conveniently refilled.

- The storage system must be safe under all operating conditions, including extreme conditions resulting from automobile collisions.

- It must be able to deliver fuel to the fuel cell or engine instantly upon startup and adjust fuel delivery instantaneously to meet changing vehicle power demands.

- It must be small enough in volume not to impinge upon passenger or trunk space and light enough not to impact vehicle fuel economy. It must be sufficiently impermeable to keep hydrogen losses through diffusion low over an extended time.

- It must be able to tolerate some level of contaminants in the fuel or the storage medium.

- The processes for manufacturing, fueling, and processing waste from the system must be energy efficient and environmentally friendly. (Otherwise, the advantages of using hydrogen to replace hydrocarbon fuels are lost.)

- These requirements must be met at a vehicle operating cost comparable to that of gasoline-fueled internal combustion engine vehicle.

The current methods of storing sufficient hydrogen to power a vehicle are pressurized storage compression, liquefaction and subsequent storage in cryogenic containment, or storage in a complex or chemical hydride. Of these, compression is the most mature and likely to be the system of choice for early generations of hydrogen-powered vehicles. The next most mature, cryogenic liquid hydrogen storage, is notably more expensive. Research into metal and chemical hydrides is in the early stages, and much more work is required to assess their feasibility.

The main research focus is energy density. For market acceptance, a storage system must store hydrogen at sufficient density to enable a vehicle range of at least 563 km (350 miles). Energy density targets for storage systems are 4.3 MJ/L by 2005 and 5.4 MJ/L by 2010. (Gasoline systems, by comparison, are at about 14 MJ/L.) At the same time, the whole system, including fuel, containment, storage medium, and associated instrumentation, must be comparable in volume and weight to fuel systems currently used in gasoline-powered vehicles. Volumetric advances (e.g., higher-pressure tanks) often have gravimetric costs (e.g., heavier tanks), so trade-offs must be constantly evaluated and managed.

State-of-the-Art Hydrogen Storage Methods

Compressed Hydrogen

Compressed hydrogen is a straightforward storage method and will probably be the easiest to implement in the short term. Most of the 3 million natural gas vehicles now on the road use compressed gas systems. Therefore, compressed hydrogen has the advantage of existing natural gas vehicle standards and industry expertise. (A U.S. standard for compressed hydrogen is expected by the end of 2003.) The current state of the art in compressed hydrogen tanks is a carbon fiber wrap and a polymer liner. These tanks are light, robust, and already commercially available. Again, energy density is the key issue. Research is needed to address the feasibility of storage at >10,000 psi; tank strength and weight; carbon fiber cost; hydrogen permeation through tank liners; non-ideal gas behavior of compressed hydrogen (relationship of permeability to storage pressure); conformable tanks; and the feasibility of using microspheres instead of tanks as storage vessels.

The primary cost driver for compressed H_2 systems is materials costs: carbon fiber accounts for 40–50% of the system cost; and carbon fiber plus stainless steel hardware, for 90% of the cost. There are significant opportunities for materials cost reductions.

Liquid Hydrogen

Liquid hydrogen is more energy dense than gaseous H_2; estimates of storage densities for the former range from 4.2 to 5.6 MJ/L with current technology. Liquid hydrogen can be stored at about 20 K at 1 bar of pressure. Issues include the energy needed to liquefy hydrogen (about a third of its energy content), the vaporization rate, the cost of the cryogenic systems, and issues associated with refueling safety. Robotic refueling systems will be essential for safe handling of cryogenic fuel. Research focuses mainly on engineering improvements such as improved insulating material and designs. A relatively new avenue of research is the use of pressurized cryogenic tanks to enable use of both compressed gaseous hydrogen and/or liquid hydrogen, lessening the evaporation losses associated with the latter.

Metal Hydrides

Chemical bonding of hydrogen in a solid material, either adsorption onto the surface of the medium or absorption into it, is expected to offer the highest hydrogen density of the known storage methods. Key research issues for hydrides include the development of new hydride materials, reversibility, roles of catalysts or dopants, thermodynamics (pressure and temperature effects), kinetics, nonthermal systems, and capacity.

Hydrogen enters a metal hydride and occupies interstices in its structure. As the hydrogen enters the metal, heat is produced, which must be thermally managed by the vehicle. The hydrogen is released when the hydride is heated.

Fuel cell research has sparked a renewed interest in alanates—complex hydrides containing aluminum, hydrogen, and another elements—but only $NaAlH_4$ has been studied in detail so far. Almost all alanates can store 6 wt % hydrogen (the DOE target). Many can store 10 wt % (the automakers' target). However, reversibility and extraction of the hydrogen have yet to be convincingly demonstrated.

Research on metal hydrides is still in its infancy. Some areas for exploration are these:

- Discovering better dopants than titanium, zirconium, iron, and carbon (the elements on which research has concentrated so far)
- Determining what happens to titanium dopant after the dehydriding reaction
- Optimizing the process so that it is reversible to the highest capacity possible
- Determining the optimum configuration for alanate beds (e.g., thermal conductivity, expansion behavior, potential reaction of hydrogen with container materials, mitigating reactivity in case of accidents in wet weather)
- Improving the synthesis of alanates for availability and affordability
- Discovering complex hydrides other than alanates

Chemical Hydrides

Chemical hydrides react with water upon exposure to a catalyst to form hydrogen and a reaction by-product. The chemical medium is stored aboard the vehicle as a liquid, generally at ambient conditions. The Millennium Cell, based on sodium borohydride chemistry, is the most fully developed chemical hydride effort. It has been demonstrated in the Chrysler Natrium, a fuel-cell-powered minivan with a 300-mile range.

Carbon

Hydrogen storage in various carbon materials (e.g., activated carbon, carbon foam, fibers, and nanotubes) has been researched. However, volumetric density levels have been unsatisfactory. Only nanotubes seem to offer any potential for acceptable volumetric density. Research issues for nanotubes include marked variability in results among different researchers, processing uncertainties, hydrogen release temperatures, and the absence of means to produce large quantities of nanotubes of the required purity.

Advanced Concepts

In addition to the more familiar technologies, numerous advanced concepts for hydrogen storage have been proposed that offer possibilities for research and development:

- New storage materials
  - Polymers engineered to store hydrogen
  - Nanoporous inorganic/organic compounds
  - Nanoporous and mesoporous materials
  - Nanoscale surfaces engineered for hydrogen adsorption
  - Solid hydrogen
  - Clathrates

- New storage and release processes
  - Mechanochemistry
  - Sonochemistry
  - Irradiation
  - Storage associated with liquids

Hydrogen Storage Research at ORNL

ORNL has had ongoing research activities to develop sodium borohydride as a fuel source for robots for several years. These activities have focused on using sodium borohydride as an expendable source of hydrogen to power fuel cells that drive robotic systems. This work has largely been successful. However, if sodium borohydride or other chemical routes for storing hydrogen are to be successful, there must be a low-cost mechanism to recycle the spent material (i.e., in the case of sodium borohydride, to recycle sodium borate). Recent efforts have focused on developing an economically viable recycling approach for sodium borohydride that meets the Department of Energy's cost targets ($1.50/gallon of gas equivalent).

Other development activities at ORNL include the following:

- Development of alanates

- Thin-film metal hydrides

- Combinatorial chemistry of metal hydride systems

- Characterization using neutron scattering

- Development of sensors for smart compressed storage vessels

The work on alanates is investigating hydrogen absorption/desorption properties of compounds [$NaAlH_4$, $LiAlH_4$, AlH_3, $Mg(AlH_4)_2$] capable of storing up to ~10 wt % hydrogen. In this work, macroalloying, with the aim of shifting the absorption/desorption conditions closer to ambient, will be guided by thermodynamic calculations as well as by electronegativity and atomic size considerations.

The work involving in situ neutron diffraction studies attempts to elucidate answers concerning structural and thermodynamic issues about the role of hydrogen in hydrogen-containing compounds. Neutron scattering allows a more accurate determination of the position of hydrogen molecules in the structure of hydrides, the atomic displacement parameters, and bond distances—parameters related to the physical characteristics of the materials. The work is expected to provide data on atomic structure, phase transformations, and thermal expansions. As part of this project, ORNL is building a pressure cell for controlled temperature and pressure tests in situ in the neutron source. We are studying $NaAlD_4$ to verify the efficacy of the cell and to demonstrate that we can generate details surrounding the role of the H atoms in the atomic structure.

Thin films are being investigated to enhance the hydriding/dehydriding kinetics. The approach is based on the use of nanometer-thick films of hydrogen storage material on the interior surfaces of mesoporous materials with a surface area of up to 1000 m^2/g. The use of such films will enable (1) fast reaction kinetics and (2) the hydriding/dehydriding reaction to occur at temperatures lower than that observed for bulk materials.

Current commercial hydrogen sensors are impractical for use as safety sensors on hydrogen storage systems because they are too large, too expensive, or simply unreliable. The objective of the sensors project is to develop *optical* hydrogen–sensing techniques into feasible commercial sensor systems that overcome these limitations. Furthermore, the sensors will be resistant to contaminants, accurate and reliable at low concentrations of hydrogen, and capable of being inexpensively manufactured and integrated into high-pressure tanks or their liners. Three sensing methods are currently under consideration, and the most promising sensor will be selected for prototype testing. One sensor method is based on the well-known affinity for hydrogen molecules to dissociate upon electron attachment. Electrons with kinetic energies of a few electron volts are especially effective at dissociating hydrogen. Following electron attachment and dissociation, the electron remains attached to one of the two atoms, forming a negatively charged hydrogen ion. This ion can be readily detected by a simple electromagnetic device. The attachment cross section is greater at temperatures much higher than room temperature. ORNL has recently discovered that micrometer-size filaments can be exploited to rapidly heat a small volume of gas. This enhancement, when coupled with microelectromechanical systems technology, will result in an extraordinarily small, relatively inexpensive hydrogen gas sensor. A second sensor method is based on some unique photoluminescent properties of certain nanoscale phosphors. Nanoscale compounds and structures have broad applicability as sensing materials because their electronic properties are strongly influenced by their chemical and physical environment. Photoluminescence nanocrystals have been shown to be extremely sensitive to their chemical environment; their luminescence lifetimes are predictably affected by the concentration of ambient hydrogen. The lifetime measurements are thus a quantitative indicator of the concentration of hydrogen. A third sensor method is based on the recently observed phenomenon in which certain electroluminescent (EL) materials induce photoemission in gas-phase molecules. The photoemission is characteristic of the molecules and is observable even at low concentrations of the species. The origin of the photoemission is under investigation, but presently it is assumed to result from emission of ballistic electrons or from high-strength electromagnetic fields at the surface of the EL material. EL devices have many attractive attributes, such as low power consumption, exceptionally small size, and extremely long lifetimes. When these sensors are integrated into composite tanks, they will provide a hydrogen detection system that can monitor areas susceptible to leak formation or monitor the entire surface area. The preferred integration method would involve connecting sensors to an optical fiber network integrated into the tank wall or liner, such that the network provides a grid of sensors. The sensors could be situated so that each is specific to a discrete area on the tank surface. If the tank were encased in a film of plastic that was fastened to the tank surface along the perimeters of the discrete areas, the sensors would then monitor the volume of gas enclosed within the plastic. The plastic encasement would concentrate the leaking hydrogen and increase the sensitivity of the sensor system.

Summary

In summary, as noted in the *Rerum Novarum*, "in our time, in particular, there exists another form of ownership which is becoming more important than land: the possession of know-how, technology, and skill." The pursuit of knowledge of how to produce, store, distribute, and use hydrogen as a fuel is an important subset of mankind's knowledge about a future supply of a cheap, abundant, mobile form of energy. Without an inexpensive energy supply, the standard of living of peoples will not rise but instead decline. Achieving a hydrogen economy will require an international effort. Such international forums as this are not only an indication of progress toward achieving the ultimate goal of supply of abundant energy but also represent progress toward countries working together in peaceful pursuits. I congratulate this symposium's organizers and all the conference attendees in participating in a small but vital effort to achieving these goals.

I do not wish to overextend my welcome, so I will conclude my remarks. I thank you for the opportunity to share my views with you, to describe the hydrogen storage research issues, and to outline the work being conducted at Oak Ridge National Laboratory.

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