Addressing Grand Energy Challenges through Advanced Materials

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and M.V. Buchanan

Abstract

The following article is based on the plenary presentation given by Mildred S. Dresselhaus of the Massachusetts Institute of Technology on November 29, 2004, at the Materials Research Society Fall Meeting in Boston. Advanced materials offer new promise for addressing some of the grand societal challenges of our future, including that of global energy. This article will review opportunities that have opened up at the nanoscale, with materials of reduced dimensionality and enhanced surface-to-volume ratio. Some examples of research accomplishments and opportunities at the nanoscale will be described, with special attention given to the potential for advanced materials and nanoscience to have an impact on the grand challenges related to a sustainable energy supply for the 21st century and beyond.

Keywords: *advanced materials, catalysis, energy, fuel cells, hydrogen, nanoscience.*

Introduction

In the present century, we can expect major changes to occur in energy demand and in the form in which energy is supplied and utilized worldwide. The increasing demand and the concomitant diminishing availability of fossil fuel resources expected for the rest of the 21st century will create both a great societal problem on an international level and a challenge to the science community to find solutions that are technically viable and economically affordable. This article summarizes a plenary talk presented on November 29, 2004, at the Materials Research Society Fall Meeting in Boston that reviewed the grand energy challenges now facing society and discussed the role that advanced materials, nanoscience, and nanotechnology may play in addressing these challenges. The major conclusions of this article are that the grand energy challenges must be considered on a 50- to 100-year time frame, requiring major advances in both basic and applied materials research working hand-in-hand, blending physics, chemistry, materials science, and biology into an interdisciplinary experimental and theoretical goal-oriented mix. While the scientific and technological challenges are admittedly very great, strong societal demands and the motivation to maintain a desired quality of life will drive the search for societally acceptable, technically viable, and cost-effective solutions to be found within the critical time frame.[1–3]

The Grand Energy Challenges

Let us first delineate some of the grand energy challenges. Figure 1 shows data for the global demand for energy over the last 30 years of the 20th century and predictions into the first 25 years of the 21st century. This global energy-demand model shows a more than linear increase in overall demand as we look into the future.[4,5]

While the energy needs of the industrialized world increase somewhat in that time frame, the overall trend in Figure 1 is more seriously driven by a significantly larger demand from the developing world, whose populations previously consumed very little energy but will be aspiring to a standard of life enjoyed by the industrialized countries that are currently the major consumers of energy. The current energy utilization worldwide is close to 14 terawatts (expressed as power averaged over time), and by the end of the century, the energy consumption may be as much as 50 TW.[5] Our first grand challenge will be to find a technically viable and socially acceptable source capable of supplying this more than threefold increase in energy demand.

Today, more than 80% of the world's energy comes from fossil fuels. As the expected fossil fuel supply is depleted[6] (see Figure 2), a shift to renewable energy sources by the middle of this century is expected to occur. Earth-based renewable sources such as hydroelectricity, wind, tides, geothermal, and biomass are expected to fall significantly short of the total demand. Only the sun, with its 165,000 TW of energy bombarding planet Earth, can supply the large amount of energy that will be required by the global population of ~10 billion that is expected by the end of the century. Thus, the second grand challenge is to define and implement a strategy to make a transition by 2100 from a fossil fuel economy to renewable energy sources powered by the sun, with solar photovoltaic, solar thermal, wind, hydroelectric, and photosynthesis energy contributing to the mix.

As the shift to renewable energy sources occurs over the next 50–100 years, it is likely that the strategies adopted for the intermediate time frame will differ significantly from country to country, depending on local conditions. We can expect countries like the United States, with its large coal reserves, to emphasize clean coal-reforming technologies for the intermediate time frame, while countries like Brazil, with its large biomass capability, are likely to emphasize approaches such as sugarcane conversion to alcohol as an energy source. For countries where neither coal reforming nor biomass conversion is feasible, the option of fission (or possibly fusion in the future) will become increasingly necessary for the interim period.

Emphasis on the preservation of the environment is expected to become of increasing importance, particularly the avoidance of undesirable climate changes brought about by present patterns of human energy consumption, which produce large amounts of CO_2 and particulate emissions. The mean worldwide temperature rise in the last 300 years is arguably on the order of 1°C; the increase in atmospheric CO_2 content is arguably 20 ppm over this time period, which is small on the scale of the long-term effects over hundreds of thousands of years, as suggested by Figure 3. Over the approximately 100 thousand-year cycles that have been documented by ice cores and other geological studies,[7,8] we see mean-value temperature cycles of 10°C and atmospheric CO_2 cycles of over 100 ppm, giving us comfort that the Earth has a significant climatic elasticity that we have not yet exceeded. On the other hand, Figure 3a shows that we are very close to the edge of previously tested ranges of climatic stability. Based on past experience, we could expect a turning point to lower mean temperature in the oscillatory behavior shown in Figure 3a. The experience of the last 300 years, however, shows an increasing trend in mean temperature and atmospheric CO_2 that could take us outside the historical stability range of this oscillatory behavior. Such an excursion could provoke unstable or chaotic atmospheric effects. This would argue for the wisdom of adopting energy strategies that keep the planet within the stability ranges suggested by Figure 3.

As we move into the 21st century, many countries around the world have become increasingly concerned about these grand energy challenges and are committing resources to address the interdependent challenges implied by increasing energy demands, dwindling supplies, and environmental concerns. The United States is among the nations taking steps to address this challenge, as indicated by the launching of two new and partly interrelated initiatives: the Hydrogen Fuel Initiative and the National Nanotechnology Initiative (NNI). Substantial federal support for these two initiatives is necessary because of the magnitudes of these grand energy challenges, the high-risk research that is involved, and the continuing quest to identify the best technical approach for addressing them.

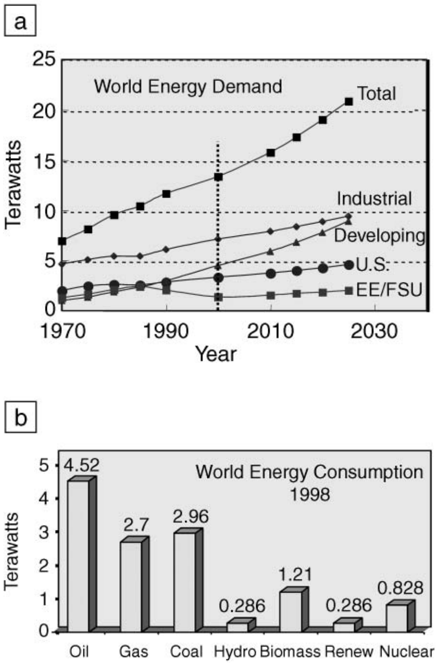

Figure 1. The challenge of world energy use, showing (a) past and predicted world energy demand in terawatts (TW), and (b)1998 consumption in TW of various fuel types.[4,5]

Many scientists see an opportunity for advanced materials, nanostructures, and nanotechnology to play a significant role in addressing the grand energy challenges (e.g., see the article by R. Smalley in the June issue of *MRS Bulletin*). Funding for the NNI started in FY00, while funding for the Hydrogen Fuel Initiative started with the FY04 budget for applied R&D, with basic research included in the FY05 budget. This review focuses on how advances in materials research and development can work to address the grand energy challenges we face.

Advanced Materials to Address the Grand Energy Challenges

About 30 years ago, when energy prices shot up rapidly and energy availability decreased due to the oil crisis of the early 1970s, a flurry of materials research activities sprung up in industrialized countries to address long-term sustainable energy goals. But when low oil prices returned by the end of the 1970s, energy-related materials research projects rapidly lost popularity. In the meantime, materials research overall has rapidly advanced, bringing us much new knowledge and capability, with much more promise for making progress toward addressing the grand energy challenges we have outlined. During the three decades since the oil crisis, we have learned a great deal about nanostructures, catalysts, membranes, theory and simulation, biomaterials, and a host of other topics of relevance to energy needs. We review a few examples of the advances made in materials research during this time period that offer promise for energy-related applications.

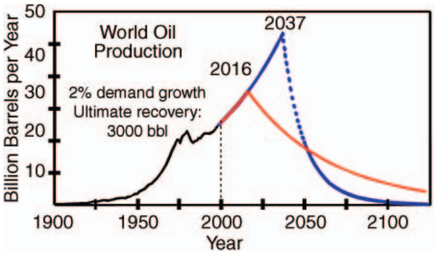

Figure 2. The challenge of dwindling world oil supply for two scenarios of oil production and consumption (bbl = billion barrels).[6] The red curve assumes that production grows at 2% per year and then declines at the same rate, producing a peak in 2016. The blue curve assumes that production grows at 2% per year until it reaches 10% of reserves, and then declines while maintaining the same ratio. The area under both curves is the same, equal to total estimated reserves.

One recurring theme in energy-related research is the need to find better catalysts that will lower the energy barrier of a chemical reaction to efficiently yield a specific energy product. Nanomaterials have revolutionized the science of catalysis by providing new methods for producing catalysts with more accessible surface area, and for controlling their crystallographic structure, size, shape, alloy content, and array organization. Nanostructures also provide special catalyst support

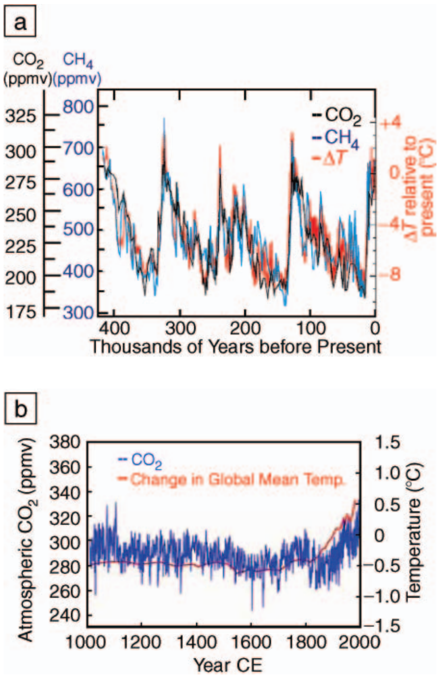

Figure 3. The challenge of climate change, giving (a) the long evolution (over thousands of years) of CO_2 and CH_4 atmospheric gas concentrations and of the change in mean global temperature relative to the present, and (b) the data for atmospheric CO_2 and the change in mean global temperature for the last thousand years.[7] The unit ppmv is parts per million by volume.

structures and self-assembled arrays of pores to effectively house arrays of chemically accessible catalytic particles. It is not only the increased available surface area that nanotechnology brings to catalytic performance, but also new desirable properties not present in their bulk counterparts.

Many materials acquire new chemical properties at the nanoscale, related to the size-dependence of their electronic structure. For example, gold in bulk form is not chemically active, but at the nanoscale, a gold particle 3 nm in size is highly active chemically, and therefore gold nanoparticles have become promising catalytic particles for inducing chemical reactions, like the oxidation of CO, of importance to energy-related research. To tailor a catalytic particle for a specific application, other elements may be combined within the particle to provide an excellent handle for controlling the properties of the reaction products; this approach can be used in addition to controlling the size, shape, orientation, and temperature of the catalytic particle.

In recent years, theory and simulation based on density functional approaches have played an increasingly important role in the selection and design of catalytic particles. These computational tools were not available 30 years ago, when computer capability was quite primitive by comparison to today. The objective of current research is to develop efficient catalysts that are highly selective of a particular desirable reaction while suppressing competing reactions, and that are also easily synthesized in a highly reproducible way, low in cost, and capable of scale-up for mass production.

Nanostructures allow materials to exhibit many new and desirable energy-related properties not displayed by their bulk counterparts. For example, thermoelectric performance is enhanced by increasing the ratio of the electrical to thermal conductivity. Nanoscale structures do this in two ways, first by introducing boundaries designed to scatter phonons much more efficiently than electrons, and second by increasing the density of electronic states through quantum confinement effects followed by doping to place the Fermi level at a peak in the density of states. These nanostructuring effects allow continuous tuning of the bulk thermoelectric performance over wide ranges.

In some materials, however, nanostructuring produces qualitative changes in the thermopower performance that are potentially much more dramatic than the tuning effects just described. For example, bismuth has highly desirable thermoelectric properties, such as its high electrical conductivity (and low effective mass) along certain crystallographic directions and a reasonably high density of states due to high effective masses along other crystallographic directions. Such anisotropic properties, along with the numerous electron and hole carrier pockets in the Brillouin zone and a very low thermal conductivity, give rise to potentially excellent thermoelectric properties. Bi, however, is a semimetal with an equal number of negatively charged electrons and positively charged holes that nearly cancel each other's contribution to the Seebeck and Peltier coefficients that control the conversion between thermal and electrical energy. Quantum confinement removes this near-cancellation qualitatively by transforming Bi from a semimetal to a semiconductor.

In the quantum-confined limit, Bi forms electronic subbands from the small number of discrete electronic states in the directions along which the sample is quantum-confined. As the sample size decreases along these directions, the lowest-lying conduction subband increases in energy, while the highest-lying valence subband decreases in energy. Eventually, at some critical sample size, the valence- and conduction-band extrema cross, and the semimetal is converted into a semiconductor, as shown in Figure 4. For a Bi nanowire at 77 K, the semimetal–semiconductor transition occurs at a wire diameter of about 50 nm. In the semiconducting phase, Bi in Group V of the periodic table can be doped *n*-type by the addition of a Group VI dopant such as Te, or *p*-type by adding a Group IV dopant such as Sn. Thus, Bi nanowires can be used for either the *p*-type leg or the *n*-type leg of a thermoelectric device.[9] Further control of the electronic properties of Bi can be achieved by adding isoelectronic Sb to Bi.[10] Such isoelectronic doping is especially important for thermoelectric applications as a means of preferentially enhancing phonon scattering by a chemically random lattice, while having little effect on the charged carrier electronic transport.

Nanotechnology is likely to have a large impact on reducing energy demand in residential and commercial lighting, as the light-emitting diode (LED) enters the marketplace as a white light source. The LED, discovered in the 1960s, is a device in which electrically excited electrons emit light when they recombine with the holes left behind. The luminous performance of the LED, defined as the emitted light power relative to the electric power expended in the carrier excitation, has increased dramatically, and has even shown a Moore's law behavior over the past 30 years. Whereas early work involved red light emission by relatively small-gap semiconductors, the rapid development of the green and blue LEDs in the 1990s has allowed the development of white LEDs suitable for general lighting purposes (see the article by Holonyak in this issue). As shown in Holonyak's article, the efficiency of LEDs has already surpassed that of halogen incandescent lamps.[11] Promising new developments, such as the incorporation of quantum dots into the quantum wells of the heterostructure of the LED to increase the quantum effi-

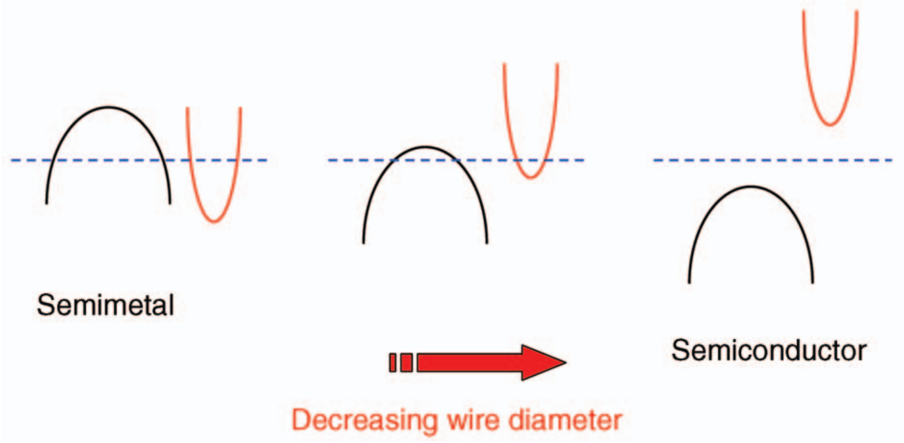

Figure 4. The semimetal–semiconductor transition as a function of nanostructure size.[9] The parabolas represent the valence (black) and conduction (red) bands of the electronic structure; the dotted blue line represents the Fermi energy separating occupied energy levels from unoccupied energy levels. As the size of the sample decreases, the bulk semimetal electronic structure transforms to a nanoscale semiconductor electronic structure.

ciency, together with the use of photonic-crystal architectures to direct the radiation of the LED in the forward direction rather than in all directions at once,[12] are expected to significantly increase the luminous efficacy of the next generation of LEDs. In addition, large savings in power are expected to come from the use of LED lighting devices to illuminate only those regions where good lighting is needed, like the operating table in a hospital or the page of a book, and to use a lower level of lighting for general background use.

The incandescent light bulb was not developed by making better candles, nor were LEDs developed by making better light bulbs. In each case, revolutionary new ideas produced the major advances. This example of the benefits of nanotechnology serves to illustrate that Moore's law is possible in the energy industry, provided that there is sufficient investment in basic research to develop the innovative concepts driving new generations of energy technology. Sustained exponential progress comes from successive innovation rather than continuous incremental improvement. Sustained successive innovation is needed in the coming decades to develop the necessary technology and the engineering principles needed for the mass production of energy-related devices. Research breakthroughs producing Moore's law increases in performance are especially needed for extracting energy from renewable sources like the sun with adequately high efficiency at a low-enough cost for mass utilization worldwide.

The Hydrogen Economy

U.S. president George W. Bush, in his 2003 State of the Union address, introduced the Hydrogen Fuel Initiative as a promising direction toward addressing the grand challenge of future U.S. energy needs and offered research funding to promote its development. The authors of this article were invited by the Office of Basic Energy Sciences of the U.S. Department of Energy to direct a study of the basic research that should be undertaken to optimize the chances of success of a "hydrogen economy" to provide for our future energy needs from renewable energy sources. The study was carried out from March to July 2003, with intensive effort occurring at the Hydrogen Workshop held May 13–15, 2003, and attended by about 125 participants from academia, industry, government laboratories, and funding agencies; the workshop culminated in a widely cited report.[13]

The Hydrogen Fuel Initiative is one approach to addressing the grand challenges of future energy needs. It focuses primarily on the transportation sector, which today consumes roughly a quarter of the energy used in the United States, with another quarter being consumed by the residential sector, a third quarter being consumed by the industrial sector, and the remaining quarter being consumed by the conversion of one form of energy to another (e.g., fossil fuel chemical energy to electrical energy). The hydrogen economy, as developed in this report,[13] has three aspects: production, storage, and utilization in fuel cells, mainly for transportation applications. The study found that in each of these three areas, the gap between present scientific knowledge and that needed for a viable hydrogen economy operating in the latter part of the 21st century is so enormous that a large and concerted basic research effort is needed.

Each of the three aspects of the hydrogen economy has its special challenges (see Figure 5). Since molecular hydrogen does not occur naturally on Earth, it has to be produced from natural resources like fossil fuel or water. Today's production is at the 9×10^6 tons/yr level and comes from the reforming of various fossil fuels such as oil and natural gas. The challenge is to increase the production capacity to 150×10^6 tons/yr from renewable sources of energy to satisfy the expected needs of automobiles and light trucks in the United States by 2040. The most attractive approach would be a decentralized system of small plants, perhaps eventually in individual houses, to convert sunlight efficiently, safely, and cheaply to hydrogen from highly abundant H_2O by a catalytic electrolytic process. We currently lack the basic knowledge for designing systems to accomplish this conversion. Nanoscience is likely to play a major role in the development of highly selective catalyst particles and in bringing modeling and simulation to this problem. Bioscience will be another source of inspiration—biological systems routinely carry out these kinds of reactions with high efficiency, although on a small scale.[13]

The storage of hydrogen is considered to be a major problem because of its low volumetric density, which arises from its low compressibility. Even liquid hydrogen falls short of the U.S. Department of Energy's requirements for 2015 (see Figure 6) that are based on a reasonable size for the fuel tank of a family automobile and the distance that consumers typically travel between filling their gas tanks. In contrast to internal combustion engines, fuel cells produce useful energy without going through heat as an intermediate state, thus allowing large gains in energy efficiency to be realized. Alternative means of storing hydrogen include forming hydrides with other atoms (see Figure 7); physisorption on carbon surfaces has also been considered.[14,15] However, for use in a fuel cell to convert chemical energy to electrical energy efficiently, easy release of hydrogen from the storage medium with minimal energy consumption is needed. The laws of physics regarding binding energies make it very difficult to find a

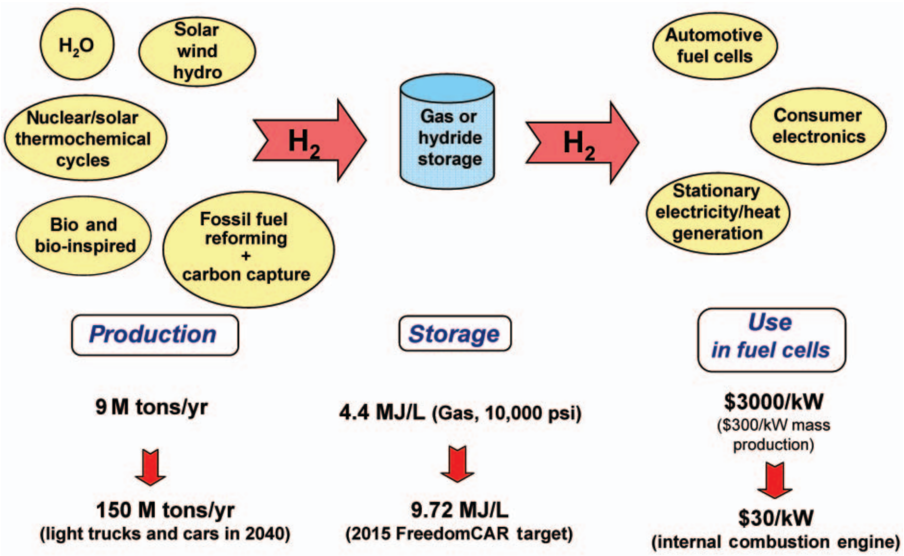

Figure 5. Technology gaps in the hydrogen economy (indicated by downward arrows) relative to hydrogen production, storage, and use in fuel cells.[13]

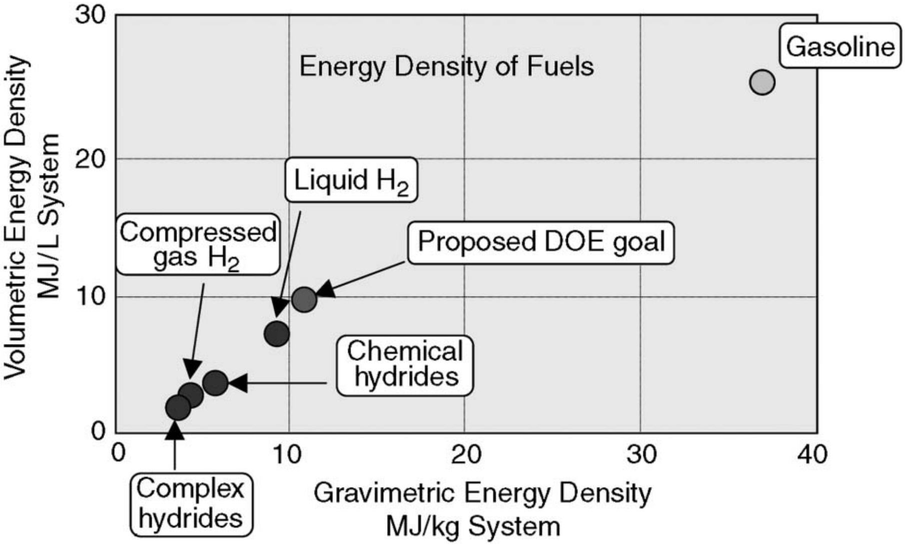

Figure 6. Volumetric versus gravimetric energy densities of various materials classes, compared with gasoline and the U.S. Department of Energy's goal for 2015.[13]

medium that simultaneously provides large hydrogen storage density and easy hydrogen release. Therefore, significant basic research will be necessary. Nanoscience is likely to play a role here as well, in providing large surface areas to promote hydrogen release and a method to dope specific atoms into a porous storage medium that can reduce the hydrogen binding energy locally near its surface. Theory and simulation will play a major role in selecting the appropriate hydrides and dopants and in determining their geometrical placement in the nanostructures to provide a suitable storage medium for hydrogen. If success is achieved, a hydrogen storage system could also be used by electrical power plants for short-term energy storage and for chemical/electrical power conversion applications, a general need for today's power generation industry.

The third component of the hydrogen economy involves the utilization of the hydrogen in fuel cells to effectively convert chemical energy to electrical energy. While efficient fuel cells have been demonstrated in the commercial marketplace, intensive research is now in progress, mostly in the industrial sector, to dramatically improve their performance and durability and to lower costs. Here, nanotechnology can contribute significantly by promoting more efficient anodes (where H_2 is converted to H^+, and electrons are released to the external circuit), more efficient cathodes (where O_2 is converted to O^{2-} and combined with protons to produce H_2O), and more efficient ion-conducting membranes operating at higher temperatures, allowing selective passage of the H^+ through the membrane from anode to cathode. More efficient, lower-cost catalysts are broadly needed to make fuel cells technically and economically competitive with today's internal combustion engine. Solving the triple-percolation problem is necessary in order to provide easy transport channels for species in three different phases—gases like H_2, O_2, and H_2O; electrons in metallic wires; and ions like H^+ or O^{2-} in ion conducting membranes—to interact at a common point with an oxidizing or reducing catalyst. Designing nanoscale architectures with such interpenetrating gaseous, electronic, and ionic channels is a fascinating challenge. Catalysis research from a nanoscience and nanotechnology perspective is needed to develop higher-performance catalytic particles of controlled size, shape, composition, and optimized placement to address the triple-percolation problem. Progress based on research now ongoing in laboratories worldwide and the experience gained from the in-service operation of fuel cells in fleets of hydrogen-powered buses and autos now under evaluation in various countries, coupled with the operation of large stationary fuel cell units for power generation in hospitals and the utilization of small fuel cell units in the electronics industry for powering portable devices like laptop computers, will give industry valuable experience with consumer needs and with developing large-scale manufacturing capabilities.

We envision a dual approach to the evolution of a hydrogen economy for the next decades (Figure 8). The experience gained with today's technologies in the production, storage, and utilization of hydrogen in fuel cells is necessary to developing the industrial capability and capacity for the large transitions expected to occur in subsequent decades of this century as the fruits of long-term basic research are harvested. If the hydrogen initiative is to succeed, deliberate and long-term investment in basic research is necessary to bring us from where we are now to where we need to be to solve the enormous problems before us. These problems include the effective production of hydrogen, its storage,

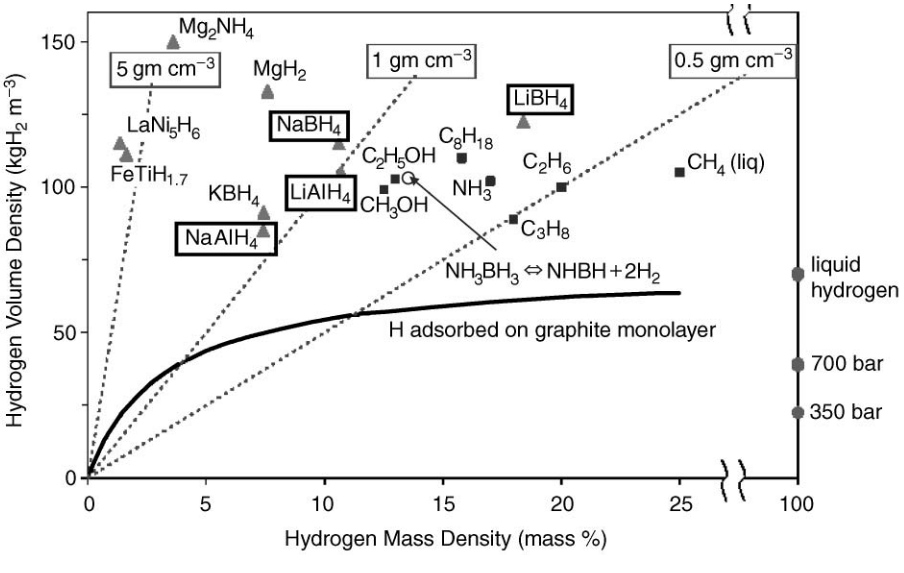

Figure 7. Volumetric versus gravimetric energy densities for candidate hydrogen storage media, including liquid hydrogen, pressurized hydrogen gas, and hydride compounds.[14]

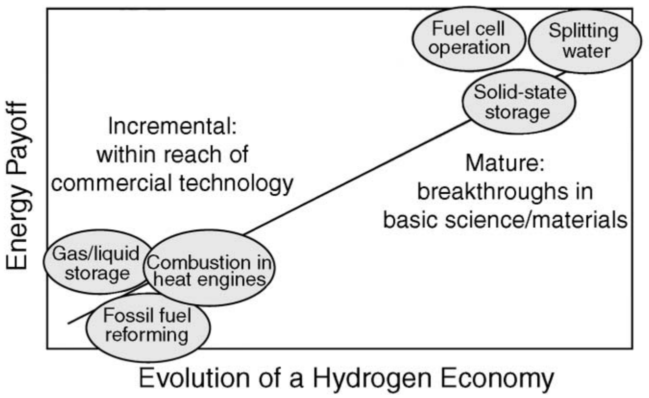

Figure 8. Evolution of the hydrogen economy from short-term R&D to long-term R&D to develop breakthrough technologies.

and its release for transportation applications and for use in hydrogen-powered fuel cells. Investments in the development of new advanced materials and nanostructures will play a vital role in the long-range energy research program and will influence and benefit from advances occurring in many related areas contributing to the development of the catalysts, biomimetic systems, nanoscale architectures, membranes, and other needed components for the hydrogen initiative.

While advanced materials research and nanotechnology has in recent years been focused strongly on the electronics, magnetics, and optoelectronics industries, now is the time to utilize the advances made in these fields to address the grand energy challenges that the world faces as the 21st century unfolds.

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