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**MASTER**

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# HYDROGEN AND THE MATERIALS OF A SUSTAINABLE ENERGY FUTURE

NATIONAL EDUCATORS' WORKSHOP

OCTOBER 28-30, 1996

PROCEEDINGS

LOS ALAMOS NATIONAL LABORATORY

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## INTRODUCTION

The National Educators' Workshop (NEW): Update 96 was held October 27-30, 1996, and was hosted by Los Alamos National Laboratory. This was the 11th annual conference aimed at improving the teaching of material science, engineering and technology by updating educators and providing laboratory experiments on emerging technology for teaching fundamental and newly evolving materials concepts. Sponsors included: U.S. Department of Energy; NASA; Norfolk State University -- Schools of Technology and Science, a historically black university; and National Institute of Standards and Technology -- Materials Science and Engineering Laboratories.

The Hydrogen Education Outreach Activity at Los Alamos National Laboratory organized a special conference theme: ***Hydrogen and the Materials of a Sustainable Energy Future***. The hydrogen component of the NEW:Update 96 offered the opportunity for educators to have direct communication with scientists in laboratory settings, develop mentor relationships with laboratory staff, and bring leading edge materials/technologies into the classroom to upgrade educational curricula. Lack of public education and understanding about hydrogen is a major barrier for initial implementation of hydrogen energy technologies and is an important prerequisite for acceptance of hydrogen outside the scientific/technical research communities.

The following materials contain the papers and view graphs from the conference presentations. In addition, supplemental reference articles are also included: a general overview of hydrogen and an article on handling hydrogen safely. A resource list containing a curriculum outline, bibliography, Internet resources, and a list of periodicals often publishing relevant research articles can be found in the last section.

# CONFERENCE PROCEEDINGS

## PLENARY

### **HYDROGEN -- THE FUEL OF THE FUTURE**

James MacKenzie, World Resources Institute

## EXPERIMENTS/DEMONSTRATIONS

*NEW participants attended conference sessions in which speakers demonstrated experiments that can be duplicated in their classroom.*

**A MODELING CODE FOR EVALUATION OF HYDROGEN POWERED VEHICLES** Salvador Aceves-Saborio, Lawrence Livermore National Laboratory and Norman Johnson, Los Alamos National Laboratory

**EXPERIMENTAL INVESTIGATION OF HYDROGEN TRANSPORT THROUGH METALS** Rob Dye and Tom Moss, Los Alamos National Laboratory

**ELECTROLYTIC PRODUCTION OF HYDROGEN UTILIZING PHOTOVOLTAIC CELLS** Mark Daugherty and Christine Zawodzinski, Los Alamos National Laboratory

## MINI-WORKSHOPS

*State-of-the-art technology at a major research facility was presented by Los Alamos National Laboratory technical staff members*

**MATERIALS FOR HYDRIDE BASED BATTERIES** Ricardo Schwarz

**HYDROGEN FUEL CELLS FOR UTILITY AND TRANSPORTATION APPLICATIONS** Shimshon Gottesfeld

**ENGINEERING MATERIALS FOR HYDROGEN SEPARATION** Rob Dye and Tom Moss

"Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable. Some day the coalrooms of steamers and the tenders of locomotives will, instead of coal, be stored with these two condensed gases, which will burn in the furnaces with enormous calorific power.

There is, therefore, nothing to fear....I believe, then, that when the deposits of coal are exhausted we shall heat and warm ourselves with water.

Water will be the coal of the future."

Jules Verne, *The Mysterious Island*. 1874.

"Fossil fuels are merely part of the 'natural capital' which we steadfastly insist on treating as expendable, as if it were income, and by no means the most important part. If we squander our fossil fuels, we threaten civilization, but if we squander the capital represented by living nature around us, we threaten life itself."

E.F. Schumacher, *Small is Beautiful*. 1973

HYDROGEN -- THE ENERGY CARRIER OF THE FUTURE  
Outline of Remarks at the  
National Educators' Workshop: Update 96

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Los Alamos, New Mexico  
October 28, 1996  
ABSTRACT

Energy has played a critical role in human evolution. Over the centuries, there have been major transitions from renewable sources (animals, water wheels, wood, and wind mills) to the present systems based on fossil fuels. However, current patterns of global energy use are not sustainable. Fossil fuels account for about 90 percent of world commercial energy supply. Though large, reserves of these fuels are finite and depletion will eventually limit their use. Indeed, there is growing evidence that world production of crude oil will peak early in the next century. Global climate change is a second, more immediate, factor in the non-sustainability of present energy use. The balance of evidence suggests that fuel-related emissions of greenhouse gases such as carbon dioxide, methane, and nitrous oxide are having a discernible impact on the earth's climate. To limit the concentrations of these gases, emissions will have to be reduced, not just stabilized. To keep the concentration of CO<sub>2</sub> below a doubling, major cuts in emissions -- i.e. fuel burning -- would have to occur over the coming century. Improved energy efficiency and the introduction of renewable energy sources are the most promising means for moving toward sustainable energy use. Renewable energy sources suffer from the limitations of diffuseness and intermittency. Both of these limitations can be overcome by converting renewable energy into hydrogen, a readily storable, clean burning energy carrier. The obstacles to the widespread use of solar energy and hydrogen are outlined.

# **HYDROGEN -- THE ENERGY CARRIER OF THE FUTURE**

James J. MacKenzie  
Senior Associate  
World Resources Institute

## **INTRODUCTION: THE EMERGING ISSUE OF SUSTAINABILITY**

The world's economy today is not sustainable in several important ways. In some places, agriculture is leading to impoverishment of the soils and to runoff of fertilizers and pesticides with cumulative effects of the environment. In others, underground supplies of fresh water, much of which is non-renewable over human time scales, are being depleted. Our use of non-renewable materials in our "once-through" society is not sustainable. And lastly, for several reasons, our current patterns of energy use are not sustainable. The challenge of the 21st century will be to steer the global economy onto a path that can be maintained indefinitely without damaging the natural systems on which we and the rest of Earth's passengers all depend.

## **THE UNIQUE ROLE OF ENERGY**

The availability of affordable energy is an essential element to global economic development. Energy is needed for virtually every important function in modern society from growing and cooking food, to manufacturing, the heating and cooling of buildings, and transportation. The interruption of supplies by storms, earthquakes, wars, or other disasters quickly demonstrates how totally dependent we have become on the energy-consuming machines that shape and support our lives. Unlike other important resources, energy cannot be recycled.

## **ROLE OF ENERGY IN EVOLUTION**

### **#1 Milestones in Energy Evolution**

Energy has played a crucial role in the evolution of the human species. Fire was harnessed some 250 to 500 thousand years ago and allowed cooking of food and movement to colder climates. In addition to wood, various other forms of energy have been harnessed over the past few tens of thousands of years including domestic animals, sails to power ships, wind machines, and water wheels.

### **#2 Evolution of Human Energy Use**

The energy budget of our ancestors, gatherers and hunters, was some 2000 to 3000 calories per person per day. The growth in per capita energy use can be seen in figure #3. In a modern industrial society food accounts for a small fraction of total energy needs, about one percent, though the energy to grow, process, and cook it increases this slightly. There are many people today living at the level of the "gathering" or "primitive agricultural" stage. Their principal energy source is wood and about 2 billion out of the earth's estimated 6 billion people rely on this source to meet most of their energy needs. Wood is the most widely used fuel worldwide. In many developing countries -- especially in Africa -- people meet 90 percent of their energy needs with biomass such as animal dung, fuel wood, and agricultural residues.

Coinciding with the end of the most recent ice age, some ten thousand years ago, humankind began to farm, allowing higher food production and the establishment of settlements. Gradually, per-capita energy consumption increased through the widespread diffusion of various forms of renewable -- if not sustainable -- energy.

Modern industrial people consume energy at a rate equal to about 100 times our dietary needs. In effect, we have 100 energy industrial servants working for us in the form of electric power plants, internal combustion engines, air conditioners, stoves, and so forth. In a cruel reversal it now appears that -- unless major changes are soon made in the forms and uses of energy -- uncontrolled energy consumption may also lead to far-reaching, possibly irreversible, damaging changes in the earth and its climate and to the widespread jeopardy of many forms of life itself.

### #3 Transition Among Energy Sources

Until about the middle of the 19th century, the world was powered almost totally by renewable resources:

- wood for heat, steam engines, and smelting of metals;
- water wheels, wind mills, sailing ships, and animal power for transportation and mechanical energy.

In 1870 there was one horse or mule in the United States for every four persons. Horses and mules in the United States numbered 25 million in the early 1900s. There are only a few million today.

The energy demands of the industrializing countries of the 19th century grew rapidly and could not be met, at the conversion efficiencies then common, with the renewable resources then available. The steam engines of the past century converted at best a few percent of the energy in wood into useful work. And trees are very inefficient "solar collectors," capturing far less than one percent of the energy in the sunlight falling on them. Fireplaces were notoriously inefficient. The lesson here for us is clear: if we are to propose using renewable energy sources, we must use energy very, very efficiently.

With the reduced availability of wood and whale oil (for lighting), and the inability to concentrate large amounts of energy on the part of water wheels, windmills, and animals, the stage was set for a transition from the renewable technologies of the day to the more concentrated and more readily available forms of energy: the fossil fuels.

Over the past one hundred years two major transitions among energy sources (excluding animal power) have occurred. The first was from wood to coal, beginning in the middle of the 19th century. This switch -- from a renewable energy source to a fossil fuel -- represented the first major transition in energy sources. The second transition began at about the turn of the century and is now largely completed. During this period, oil became the world's largest source of energy and, together with natural gas, displaced coal in many of its markets. In 1995, oil and gas accounted for about 63 percent of world commercial energy supply.

As the world nears the end of the twentieth century, it finds itself facing a third major transition, though it is still not certain to which combination of energy sources we will be moving: renewables, nuclear fission, or some combination. In any case, new energy forms will be necessary and hydrogen is a leading candidate for energy carrier of the 21st century.

### #4 Non Sustainability of Present System

The next transition will not be driven by an underlying shortage of fossil fuels, though, as we shall see, oil resources are more limited than generally appreciated. Still, the world has huge coal and heavy-oil resources which in principle, and at a price, economically and environmentally, could be converted and upgraded into synthetic oil and natural gas. The coming transition among energy sources will occur in response to serious problems that arise primarily from the use of energy, especially the burning of fossil fuels. They include air pollution in the form of smog and acid rain, and, especially, climate change. The question of oil resources is intimately involved with these latter two issues.

These threats to continued energy use are linked by the burning of fuels and together they point to the urgent need to reduce emissions by improving energy efficiency worldwide and, over the longer term, developing new energy sources. Let us review these issues now in somewhat greater detail.

### **ENERGY SECURITY, GREENHOUSE GASES, AIR POLLUTION: THE LINKED PROBLEMS**

The importance of petroleum products to the economic and national security of western nations was dramatically highlighted by the U.S.'s demonstrated willingness to go to war with Iraq in 1991 to ensure access to Persian Gulf oil.

Paradoxically, while the United States was willing to fight to protect petroleum supplies on the other side of the world, it has no long-term strategy to reduce national dependence on these producers by either improving energy efficiency or developing alternative energy sources. Nor, for that matter, do we have any policy to deal with any of the other threats posed by our present energy system.

Oil is by far the country's largest source of energy and accounted for about 40 percent of U.S. supply in 1995, followed by natural gas at 27 percent and coal at 24 percent. Worldwide, petroleum products accounted for 40 percent of commercial energy supply. The strategic importance of oil in powering modern economies cannot be overemphasized. For example, the world's transportation system -- vital to the functioning of industrial society -- is virtually totally dependent on oil.

Although world (reported) proved oil reserves are very large, they are still finite and non-renewable. The question of when global crude oil production might peak and start declining is most relevant to any serious long-term energy planning.

In general terms we know what will happen to global oil production. In due course, new oil deposits will become scarce and costly to develop, requiring the introduction of replacement energy sources. We will not, however, run out in some given year. What can we say about when this peaking in production is likely to happen?

#### **#5 Bell shaped curve**

The approach that I have taken to estimate the future of world oil production is patterned after that of the late American geophysicist M. King Hubbert. Hubbert observed that, first, annual production of a non-renewable resource such as crude oil can be expected to rise, hit one or more peaks, and eventually fall as the resource is depleted. And second, that the sum of annual production over all time (that is, the area under the production curve) is equal to Estimated Ultimately Recoverable (EUR) reserves.

In 1956, using consensus estimates of EUR oil in the lower-48 states (between 150 and 200 billion barrels), Hubbert predicted that U.S. crude oil production in the

lower-48 states would peak between 1965 and 1970. He hit the nail squarely on the head: in fact, it peaked in 1970.

#### #6 Production In the Lower 48 States

I have performed an analysis similar to Hubbert's and the predicted complete cycle of U.S. crude oil production in the lower 48 states is shown in graph #7.

#### #7 Cumulative Production in the Lower 48 States

If annual production follows a bell shaped curve, then cumulative production should follow an S shaped logistic curve. A fit to lower 48 cumulative production is shown in this figure and it is from this curve that the EUR for lower 48 states is estimated at 189 billion barrels. Note the essentially perfect fit to the data over 60 years: through world wars, local wars, economic recessions, and fairly wide swings in oil prices.

#### #8, 9 (Annual and Cumulative Production in Alaska)

The same kind of analysis can be carried out for Alaskan production where an ultimate limit of only about 15 billion barrels is inferred.

### **ESTIMATES OF ULTIMATELY RECOVERABLE (EUR) CRUDE OIL**

Over the past fifty years, many oil companies, geologists, governments, and private corporations have performed scores of studies of EUR global crude oil. (EUR oil is the total amount of oil that will eventually be pumped from the earth.)

#### #10 Estimates of EUR

Estimates made from the 1950s on, plus those from several other recent studies, taken together, reflect a consensus among oil resource analysts that EUR conventional oil resources lie within a fairly narrow range of 1,800 to 2,200 billion barrels. As of the end of 1995, the world had consumed about 765 billion barrels of these ultimately recoverable reserves.

### **LIKELY FUTURES FOR GLOBAL CRUDE OIL PRODUCTION**

Given these estimates, and assuming moderate growth in global oil demand -- about 2 percent per year -- it is straightforward, using a simple depletion model, to estimate when production of conventional crude oil might begin to decline as a result of resource constraints. To evaluate the sensitivity of the year of peaking to the amount of EUR oil, I assumed an array of values for EUR oil from a low of 1800 billion barrels to a high of 2600. I fitted simple curves whose areas correspond to these values and whose production matches 1994 and the value predicted by DOE for the year 2000.

#### #11 5 Scenarios

This figure shows that the expected year of peaking is remarkably insensitive to the assumed amount of ultimately recoverable oil. At the low end, for EUR oil equal to 1800 billion barrels, peaking could occur as early as 2007; at the expected high end (2200 billion barrels), peaking could occur around 2013. An implausibly high 2600 billion barrels for EUR oil would postpone peaking only another five years -- to 2019.

Evaluating these conclusions, some might argue that there are insufficient financial incentives to explore for new oil fields because world proved reserves are already quite ample. In effect this argument is that EUR oil is far greater than implied in the dozens of estimates shown in #11. After all, with reported proved reserves of a 1000 billion barrels and annual production of 22 billion barrels, they argue, global oil reserves should last some 45 years. In a world awash in oil, why go looking for more?



#### Preserve/production (R/P) Ratio of 45 Years

Unfortunately, a R/P ratio of 45 years in no way implies that production can be held constant for 45 years. Oil does not flow freely at a constant rate from a large container marked "proved reserves." Rather, each field has an optimal range of production (depending on the size of the oil field, remaining reserves, and other considerations) which, if continuously exceeded, will jeopardize the field's long-term productivity. In short, maintaining production at a constant annual requires continual additions to reserves.

### ROLE OF HIGHER PRICES

Others may argue that as oil scarcity takes hold, prices will rise, creating greater incentives and encouraging the use of new technology to find new oil fields and increase recovery factors. This is certainly true. But, the record of both U.S. and global oil exploration shows only marginal results.

When world oil prices were high, from 1974 through 1985, the number of exploratory and development wells in the United States increased dramatically, from 28 thousand in 1973 to a peak of 90 thousand in 1981. A high level of exploratory activity persisted until world oil prices crashed in 1986. Yet, during this entire period, proved reserves in the lower-48 states declined, from 25 billion barrels in 1973 to 20 billion in 1986. Crude oil production declined by 24 percent. Presumably, reserves and production would have declined even faster had oil prices remained low.

The lower 48 states represent the most explored real estate on earth. According to the Department of Energy, as of 1986, about 80 percent of all the wells ever drilled worldwide (about 2.9 million) were drilled in the United States. The chances of finding large new oil fields, at least in the lower 48 states, are slim. Indeed, the success rate in finding new oil in the United States has continued to decline over the past 2 decades, from 17 barrels per foot drilled in the 1970s to about 8 barrels in the 1980s. With declining exploration and lower finding rates, U.S. proven reserves have dropped by 17 percent since 1977.

Worldwide, during the 1970s and 1980s, global exploration by national oil companies increased dramatically with few new giant fields found. According to Shell International, "Although world reserves have risen by 65 per cent since 1970, nearly all of these giant fields were discovered before that date."

It is not surprising that few new giant oil fields are being found. Indeed, according to the USGS, global discovery of new oil fields peaked in 1962 and has been declining since. And it is in the giant oil fields that most of the oil is found. The one percent largest oil fields contain three quarters of all recoverable oil. The largest 3 percent of fields contain 94 percent of all discovered oil. At the other end of the spectrum, the 39,833 smaller fields (97 percent) contain only 6 percent of the crude oil that will ultimately be recovered.

If most of the giant oil fields containing most of the oil have already been found, then accelerated exploration will, at best, identify only the few remaining major fields and a larger number of smaller ones. While helpful, these smaller fields will not be able to offset the long-term exhaustion occurring in the relatively small number of very large fields. Increased recovery factors in older fields will also help slow the decline in

production; including higher estimates of ultimately recoverable oil, as we have done here, is one way to represent this effect.

No one knows, of course, what will happen year by year to world oil prices or global oil demand. But peaking of production early in the next century seems certain if the majority of oil estimates made over recent decades prove even roughly correct and if crude-oil consumption continues to rise moderately as expected. Under projected trends, world crude-oil production will begin to fall within years, not centuries, so decision-makers must reckon with the inevitable and begin introducing replacement energy sources as soon as possible.

Hydrogen, as an energy carrier, could play an important role in this coming transition, **especially in the transportation sector.**

## GLOBAL WARMING

### #12 Cartoon of Greenhouse Effect

Energy use threatens the global environment through an enhanced greenhouse effect. Greenhouse warming occurs when a blanket of atmospheric gases allows sunlight to penetrate to the earth, but partially traps the earth's radiated infrared heat.

Some greenhouse warming is both totally natural and necessary. The earth's natural greenhouse effect is largely the result of water vapor and carbon dioxide. Without it the earth would be about 60° F colder and life as we know it would not be possible. Mars has a very thin atmosphere with few greenhouse gases and maintains a temperature of -53° C (-63° F), while Venus suffers from a "runaway greenhouse effect," and has an average temperature of 447° C (840° F). Like Goldilocks and the 3 bears, the earth is in between Mars and Venus. It is "just right" for life.

It was the great French mathematical physicist Jean Fourier who argued in 1827, that the atmosphere acts like the glass of a greenhouse by letting in the visible rays and energy of the sun, while impeding the escape of the earth's radiant heat, or infrared radiation as it came to be known, back into space. The absorption of radiant heat was determined to depend primarily upon small amounts of water vapor (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) found in the atmosphere. The atmosphere is composed of about 1-2 percent water vapor but less than 0.035 percent carbon dioxide.

In 1896, Swedish chemist Svante Arrhenius correctly argued that the quantities of H<sub>2</sub>O and CO<sub>2</sub> then present in the atmosphere absorbed enough infrared radiation to warm the earth by nearly 33° Celsius (59° F). In the absence of these gases, he concluded, the earth would be an ice-bound, frozen planet. Remarkably, Arrhenius went on to examine what would happen if then-industrializing societies continued to expand their reliance on fossil fuels. He concluded that a doubling of atmospheric carbon dioxide would raise average global temperatures by 5.5° C, a figure he later revised to 4° C. This number is remarkably consistent with the now oft-cited range of 1.5° to 5° C.

For many years carbon dioxide was believed to be the only significant greenhouse gas that was increasing. However, about 20 years ago, scientists recognized that other gases were also trapping the earth's infra red radiation and that these gases were also accumulating in the atmosphere.

Over the past century, human activities have led to the buildup of not only carbon dioxide but other greenhouse gases including methane, nitrous oxide, and the chlorofluorocarbons (or CFCs). (It now appears that the warming of the CFCs is being offset by a cooling effect from the destruction by the CFCs of the ozone layer in the lower stratosphere.)

#13 Carbon Dioxide Trends: Emissions and Concentration.

The buildup of carbon dioxide accounts for about two-thirds of the greenhouse warming from long-lived gases. There is additional negative forcing from aerosols (biomass, losses in ozone and others).

#14 Temperature record and prediction

There is considerable debate as to whether global warming has already been observed. As shown in Figure 14, global data indicate that 1995 was the hottest year in the past century. And the next 9 hottest years have all occurred since 1980. Though the eruption of Mt. Pinatubo in the Philippines and air pollution from coal burning have offset some of the warming, up until 1991, the growth rate of warming was greater than at any other time on record.

The computer modeling of the earth's mean surface temperature -- incorporating only Green House Gases (GHGs) -- predicts higher temperatures than have been observed. But recent studies, incorporating the cooling effects of pollution, lead to much better agreement. Regional predictions of temperature changes are beginning to be more reliable as well.

There are, in addition to increasing global temperatures, a number of other indicators consistent with the advent of worldwide global warming:

- o the stratosphere is cooling, as predicted by climate models;
- o land-based glaciers are retreating worldwide;
- o snow-cover is diminishing;
- o the depth to permafrost in the Arctic is increasing (i.e. the surface is warming);
- o the oceans are rising from thermal expansion of the oceans and the melting of snow and ice and glaciers;

Enhanced global warming from the buildup of greenhouse gases is scientifically well established. But because of the number of possible feedback loops, there are still significant uncertainties about how large regional changes will be and how quickly they will occur. And it could easily be few more years before better answers to these questions are available.

## **INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE (IPCC) REPORT**

According to the 1995 assessment by the IPCC, "the observed warming trend is unlikely to be entirely natural in origin," and "the balance of evidence suggests that there is a discernible human influence on global climate."

Without question, coping with climate change will have major implications for future patterns of energy supply and demand including the nature of the fuel used in motor vehicles.

## WHAT ARE THE ANTICIPATED IMPACTS?

It is hard to predict regional impacts but some of the risks from climate change include:

- o more frequent human health impacts from higher temperatures such as heat waves;
- o more smog as temperatures rise;
- o high incidence of tropical diseases from insects and disease vectors that move to higher latitudes with the warming: these include malaria, dengue, yellow fever;
- o erosion of barrier islands and coastal beaches as sea levels rise and tropical storms intensify;
- o a substantial fraction of the existing forested areas of the earth will undergo major changes in vegetation types;
- o deserts will become more extreme, hotter but no wetter;
- o destruction of productive coastal wetlands and estuaries;
- o saltwater intrusion into coastal groundwater;
- o damages to coastal cities and infrastructures such as highways, powerplants, and sewage treatment plants;
- o intensification of the global water cycle with major impacts on regional resources
- o reduction in availability of water for irrigation, hydropower, and navigation;
- o less cooling and drinking water from rivers;
- o mixed impacts on agriculture; some potential benefits in the developed world and losses in developing countries. Some loss of agricultural production from extended droughts; and
- o more frequent forest fires.

Climate change will be one of the most important factors, perhaps the most important, affecting energy planning over the coming decades. And its implications for fossil fuel energy use and motor vehicle use, in particular, are profound. According to the IPCC, stabilizing atmospheric carbon dioxide levels will require the world to cut carbon dioxide emissions by at least 60 percent. It is clear that if one accepts the threat of global warming, major reductions in worldwide greenhouse gas emissions will have to

occur. The U.S. is the single largest source of carbon dioxide and has a responsibility to be taking the lead.

#### #15 US CO<sub>2</sub> Emissions

Yet, U.S. CO<sub>2</sub> emissions continue to grow, about 2 percent per year for the past few years. The two largest sources of carbon dioxide emission are the electric utilities and transportation. The utilities account for about a third and believe that they have little choice at the moment but to burn fossil fuels. Nuclear power is not an option at this time. Carbon dioxide emissions from the electric utilities and transportation have been growing over the years while emissions from industry and buildings have declined. This reflects the long-term trend toward electrification of the economy, on the one hand, and the total dependence of cars and trucks on cheap oil on the other.

#### #16 Global CO<sub>2</sub> Emissions are Also Growing

#### #17 Scenarios for Concentrations and Emissions

This figure shows possible pathways to stabilized CO<sub>2</sub> concentrations. Some policy makers talk of a global goal of no more than a doubling of CO<sub>2</sub> concentrations. (It is now about 350 ppm, 30 percent above preindustrial levels.) It would be very difficult to stop at less than a doubling.

#### #18 Summary of Climate Change and its Implications for Energy Consumption.

### **NEED FOR RENEWABLE ENERGY SOURCES**

#### #19 Properties of Renewables and Need for Hydrogen storage

To achieve this goal, we need to more aggressively encourage development of renewable energy technologies, such as photovoltaic, wind, solar thermal -- and the development of better energy storage technologies such as batteries, flywheels, and hydrogen. Unless Germany, the U.S., Japan, and other industrialized nations develop and use high-efficiency and solar technologies there is little hope of developing countries doing so.

While global climate change affects all fossil fuels, the oil problem is primarily a transportation problem. As a result, we need to promote more materials R&D to accelerate the introduction of more sustainable transportation technology such as battery and hydrogen fuel cell powered vehicles. Fuel cell vehicles will greatly reduce air pollution as well as greenhouse gas emissions. Interest in electric drive vehicles (EVs) has increased over the past decade, especially in Japan and Germany.

Most hydrogen today is obtained from natural gas, a depletable source. Production of hydrogen from renewable sources -- through electrolysis, direct photochemical reactions, or biomass waste gasification -- is a possible long-term source. In this case, virtually no carbon dioxide or pollution emissions would result.

Although hydrogen-fuel-cell vehicles share many of the attractive features of battery EVs, their widespread commercial use is some distance down the road. Fuel-cell technology is less mature and there is little infrastructure to support its use. Still, like battery-powered vehicles, fuel-cell powered vehicles would take us one step toward developing a sustainable energy system. Their use would cut air pollution and greenhouse gas emissions, reduce oil imports, and mitigate the threats to U.S. security. Since a national pipeline system might be needed to distribute this fuel widely, the

natural gas industry could help engineer the hydrogen economy, eventually providing the transmission and compression facilities and, perhaps, even the hydrogen itself.

#### #20 Hydrogen R&D Needs and Goals

To achieve the full benefits of renewables, hydrogen, and other energy carriers must be introduced. Research is needed to reduce production and storage costs, improve fuel cells, and identify the most practicable forms for a hydrogen infrastructure: the best ways of producing, transporting, storing, and consuming hydrogen.

We also need to help the less developing countries to use renewable and hydrogen technologies. This is where I believe the developed nations have a special responsibility.

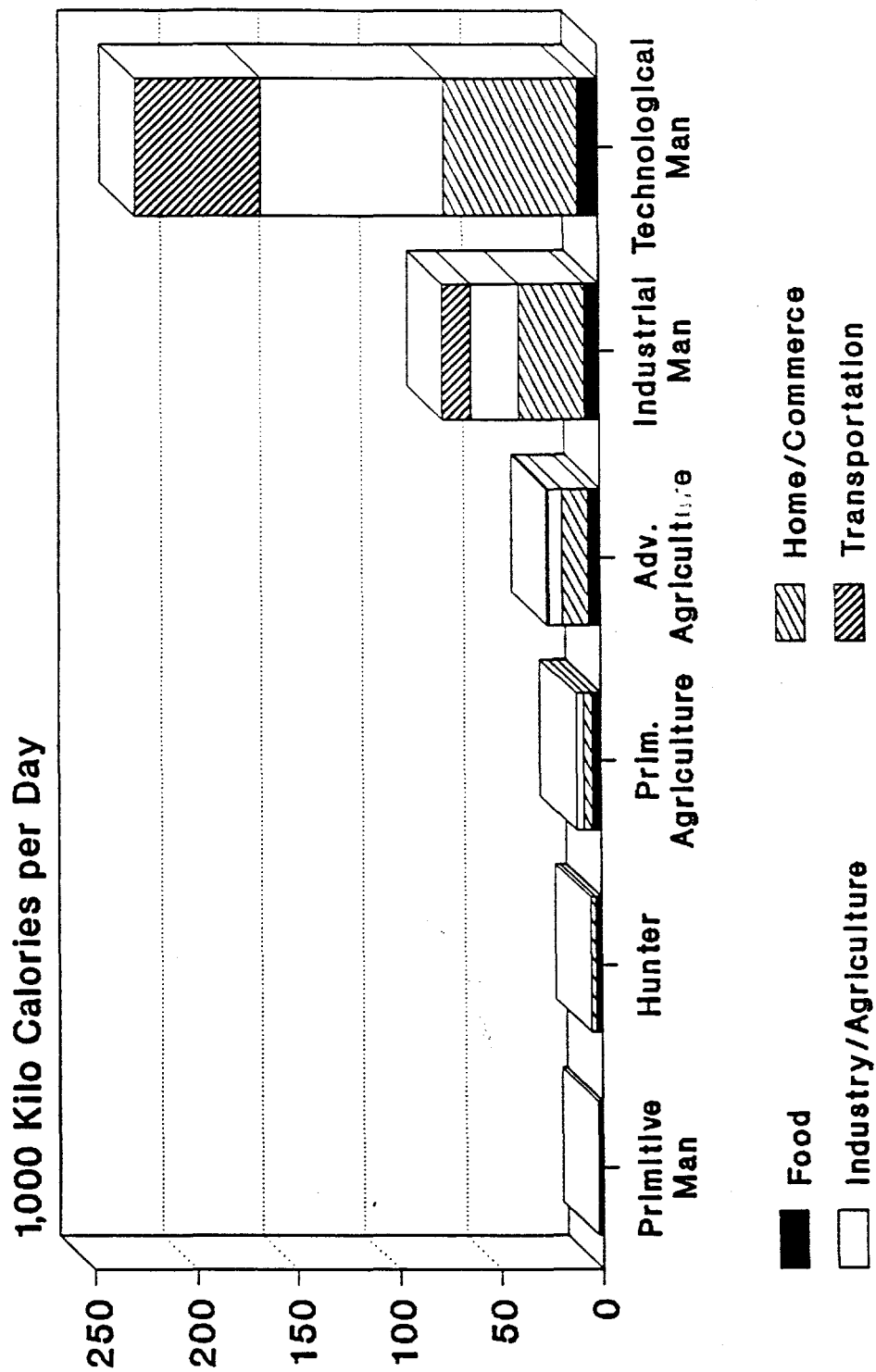
A U.S. economy structured along the lines proposed here would have a sustainable energy supply: as long as the sun shines, electricity and hydrogen would be available to power its homes, buildings, factories, and vehicles. Such an energy economy would also be self-sufficient -- reducing our need to import fuels from abroad. This would also be applicable and replicable in other parts of the world. The technologies are relatively straightforward to manufacture and are decentralized in their application. In short, renewable energy and energy efficiency together offer both the United States and the world a path to secure, clean, sustainable energy and the underpinnings for long-term economic development.

## MILESTONES IN ENERGY EVOLUTION

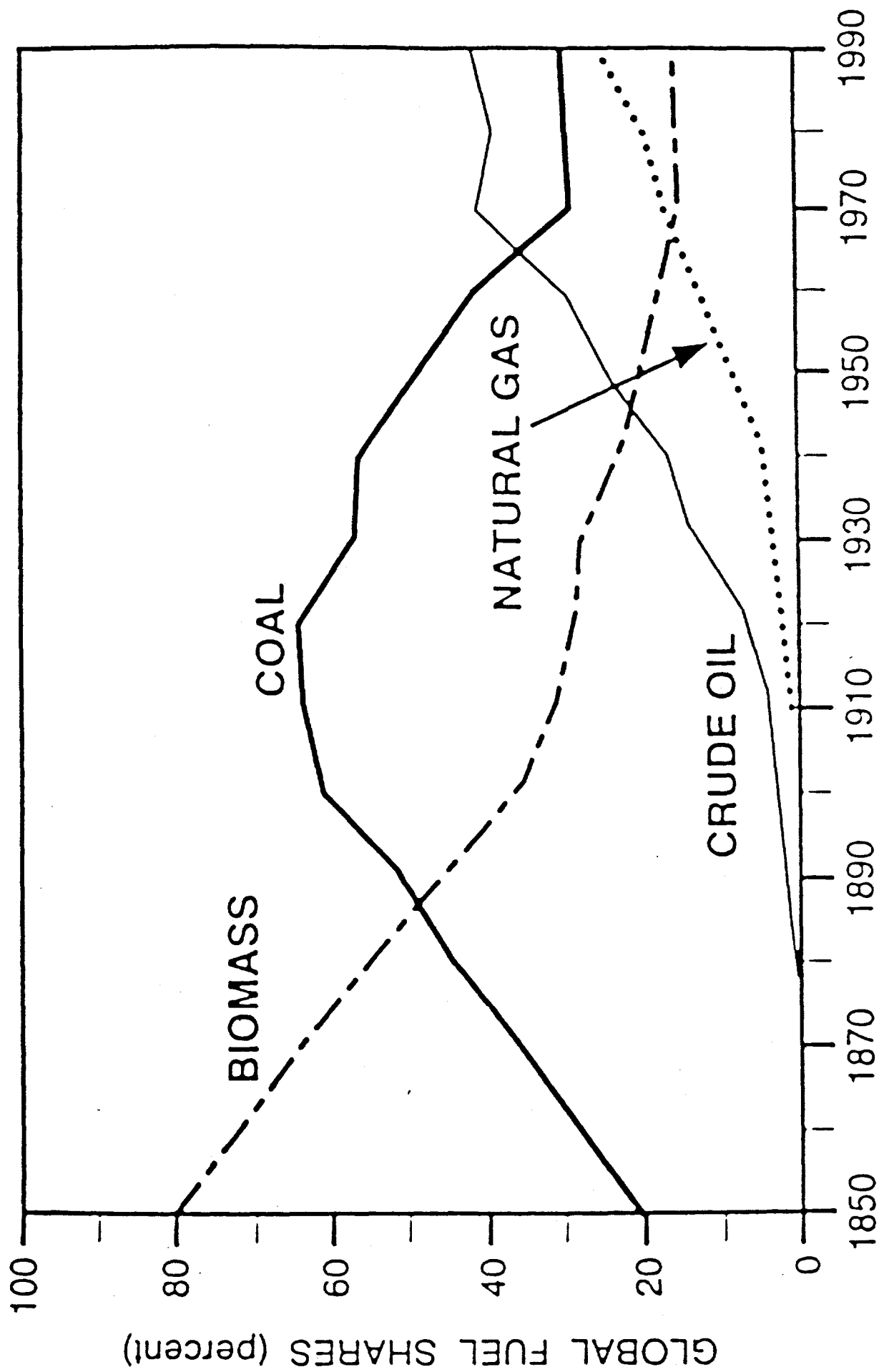
TIME	DEVELOPMENT
300-400 MYBP	Land Based Life Begins
5-8 MYBP	Mod. Man, Gatherer, Vegetarian
2 MYBP	Hunting, Tools, Ice Ages Begin
100,000-400,000 YBP	Fire, Clothing, Heating, Cooking, Migration
40,000 YBP	Weapons, Oil Lamps, Cave Art
10,000 YBP	End of Ice Age. Agriculture, Settlements, Plow, Wheels, Sails, Domestic Animals
200 YBP - Present	Motors & Engines, Coal, Oil, Natural Gas, Nuclear
Future	Renewables, Hydrogen, 2nd Generation Fission, Fusion (?)

# EVOLUTION OF HUMAN ENERGY USE

(Daily Per Capita Energy Consumption)





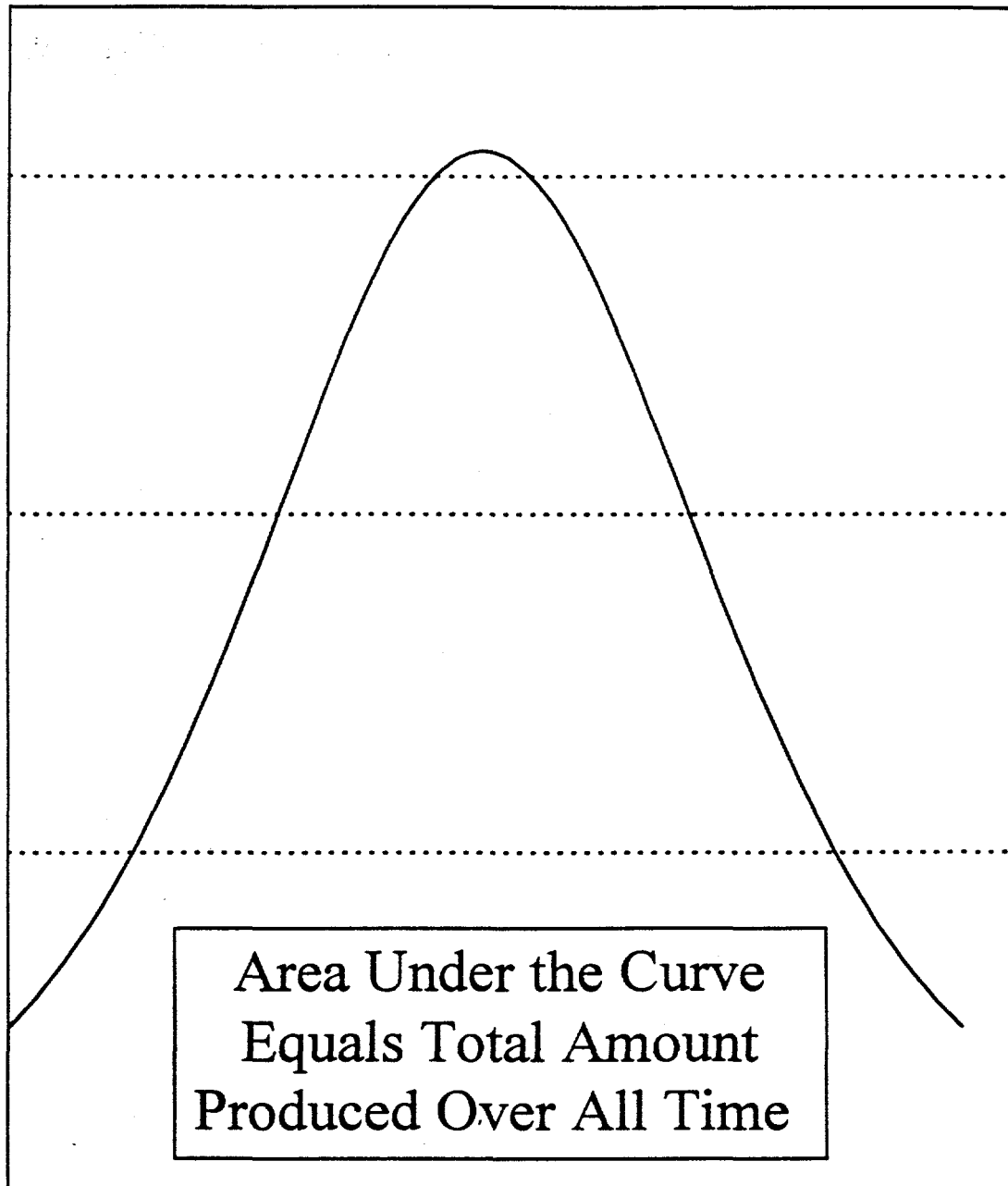


# **NON-SUSTAINABILITY OF PRESENT SYSTEM**

- **Fossil Fuels are Finite**
- **Carbon Dioxide Emissions are Threatening  
the Climate**
- **Fuel Burning Creates Air Pollution: Acid  
Rain, Smog, etc.**

# CONSUMPTION PATTERN FOR A NON-RENEWABLE RESOURCE

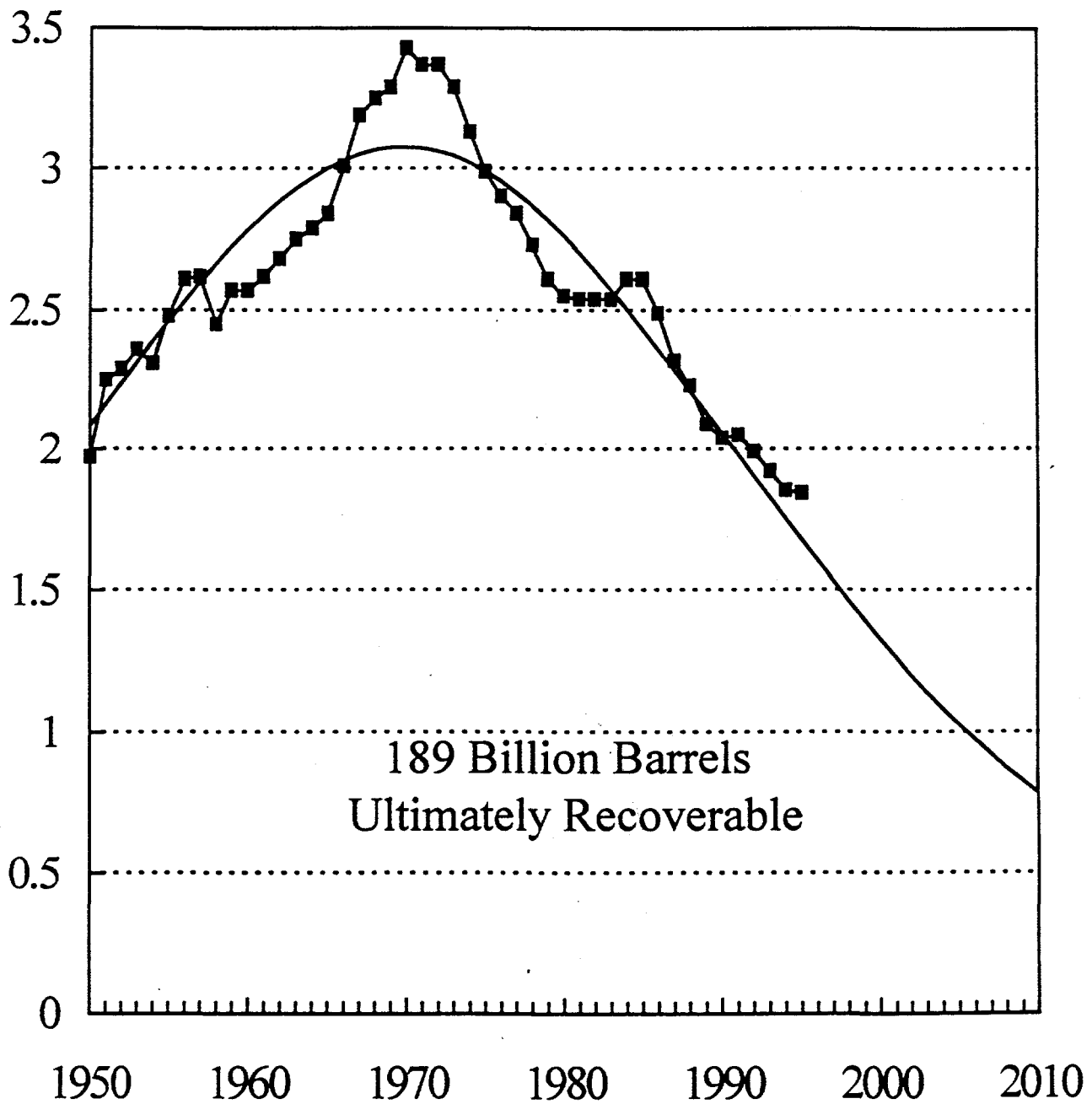
Annual Production



TIME

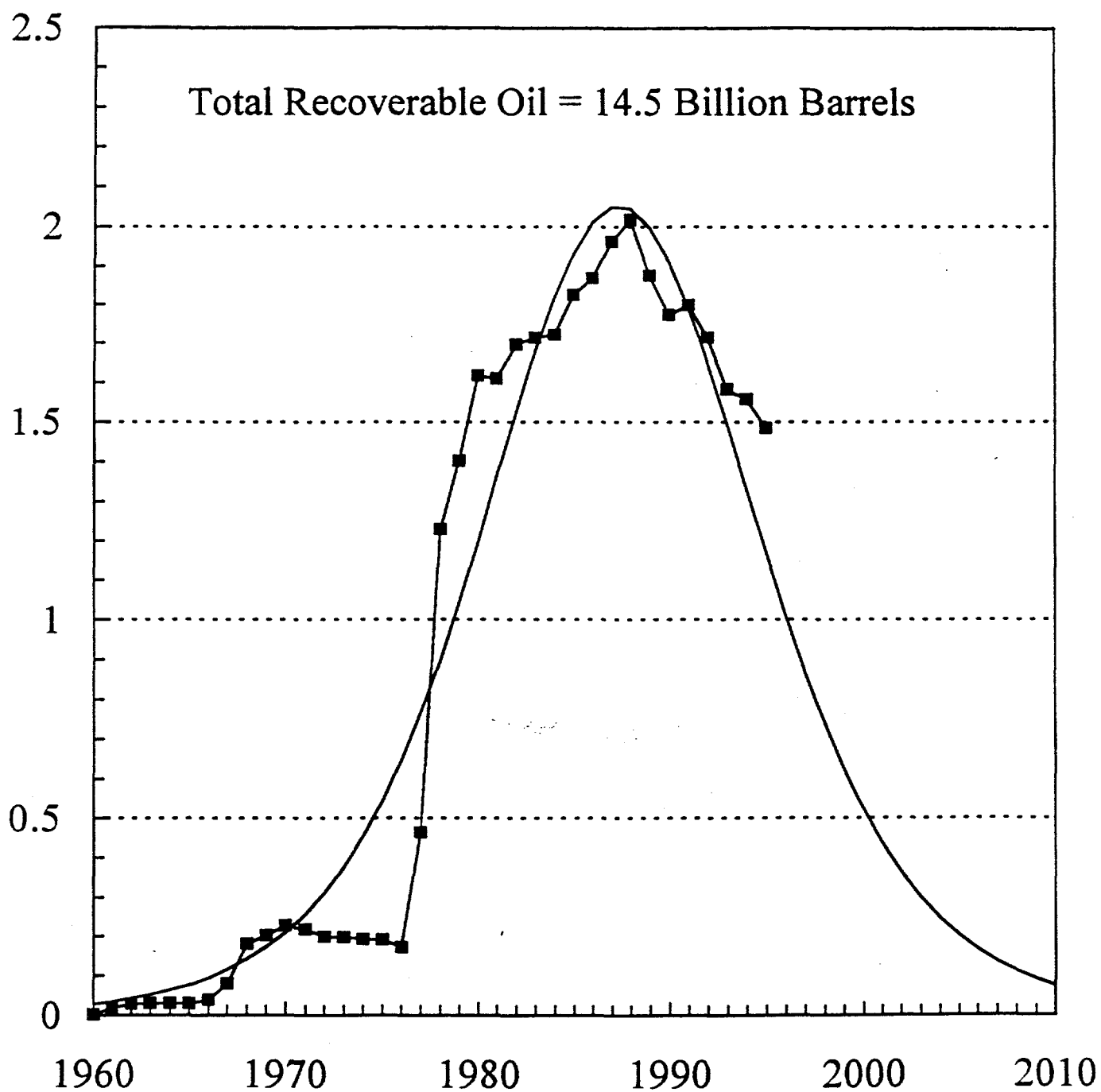
# CRUDE OIL PRODUCTION IN THE LOWER 48 STATES

Billions of Barrels per Year



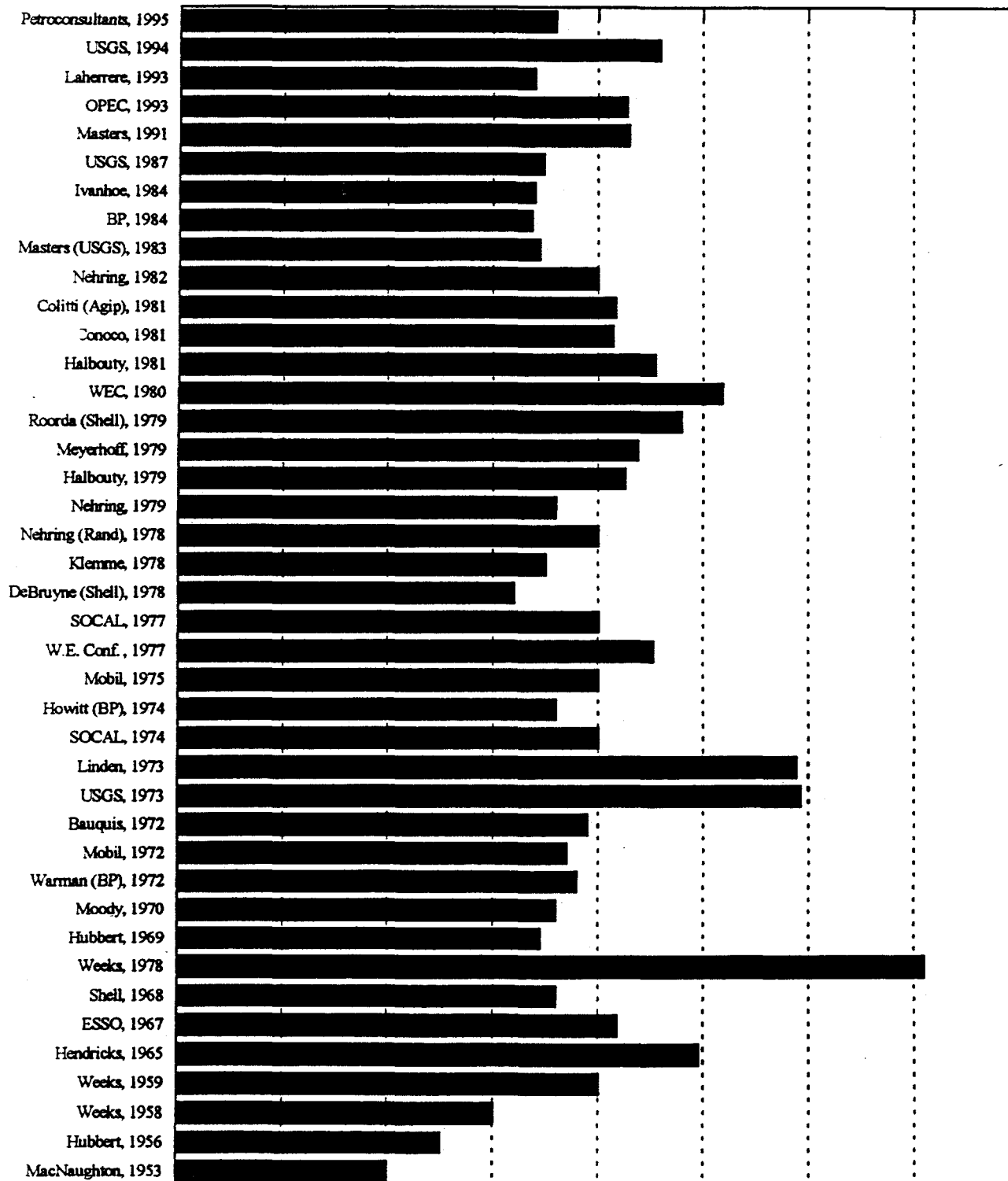
# ANNUAL CRUDE OIL PRODUCTION IN ALASKA

Millions of Barrels per Day

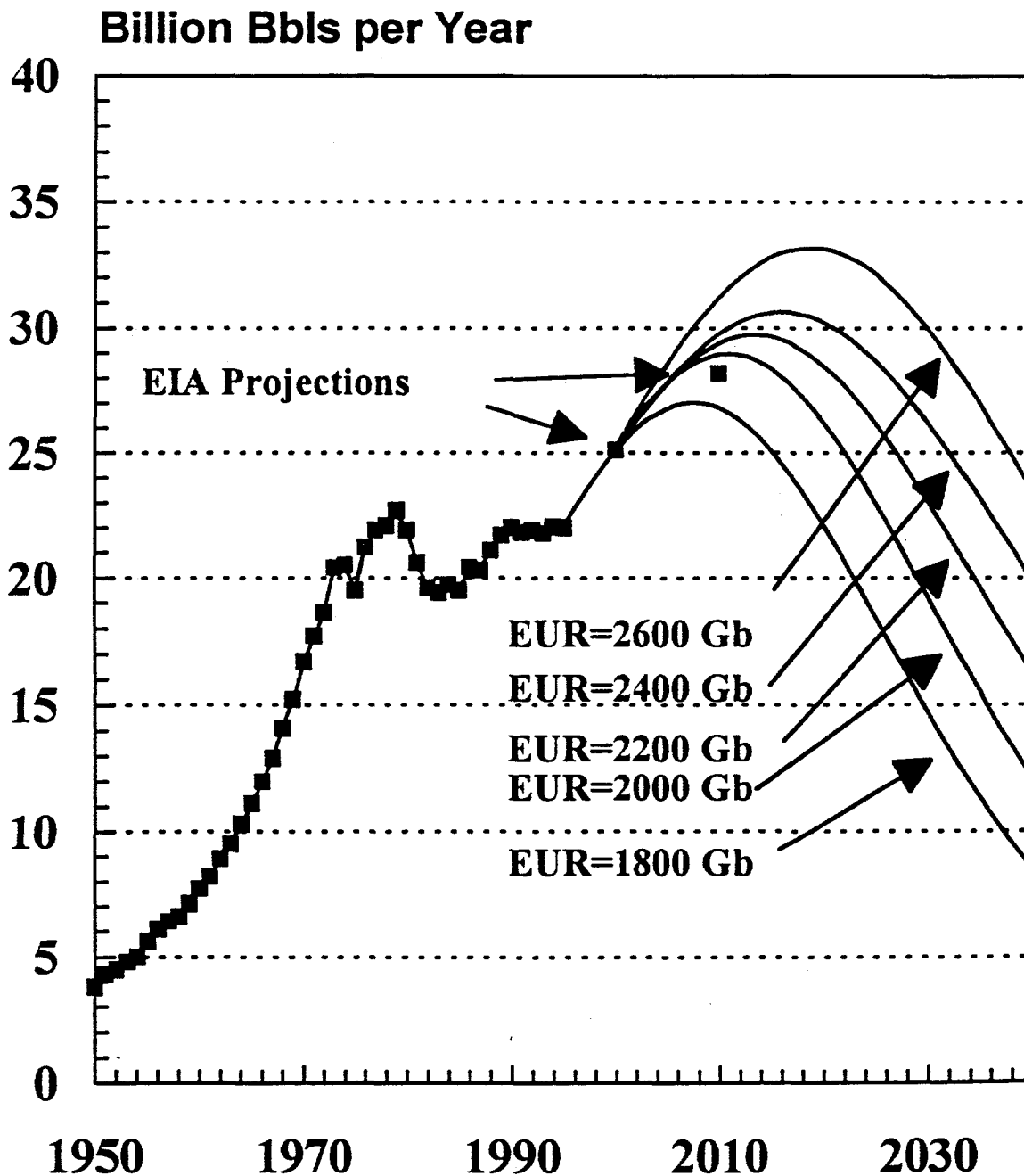


# ESTIMATES OF ULTIMATELY RECOVERABLE CRUDE OIL (Billions of Barrels)

0 500 1000 1500 2000 2500 3000 3500 4000



# GLOBAL OIL PRODUCTION FOR EUR = 1800, 2000, 2200, 2400, 2600 Gb

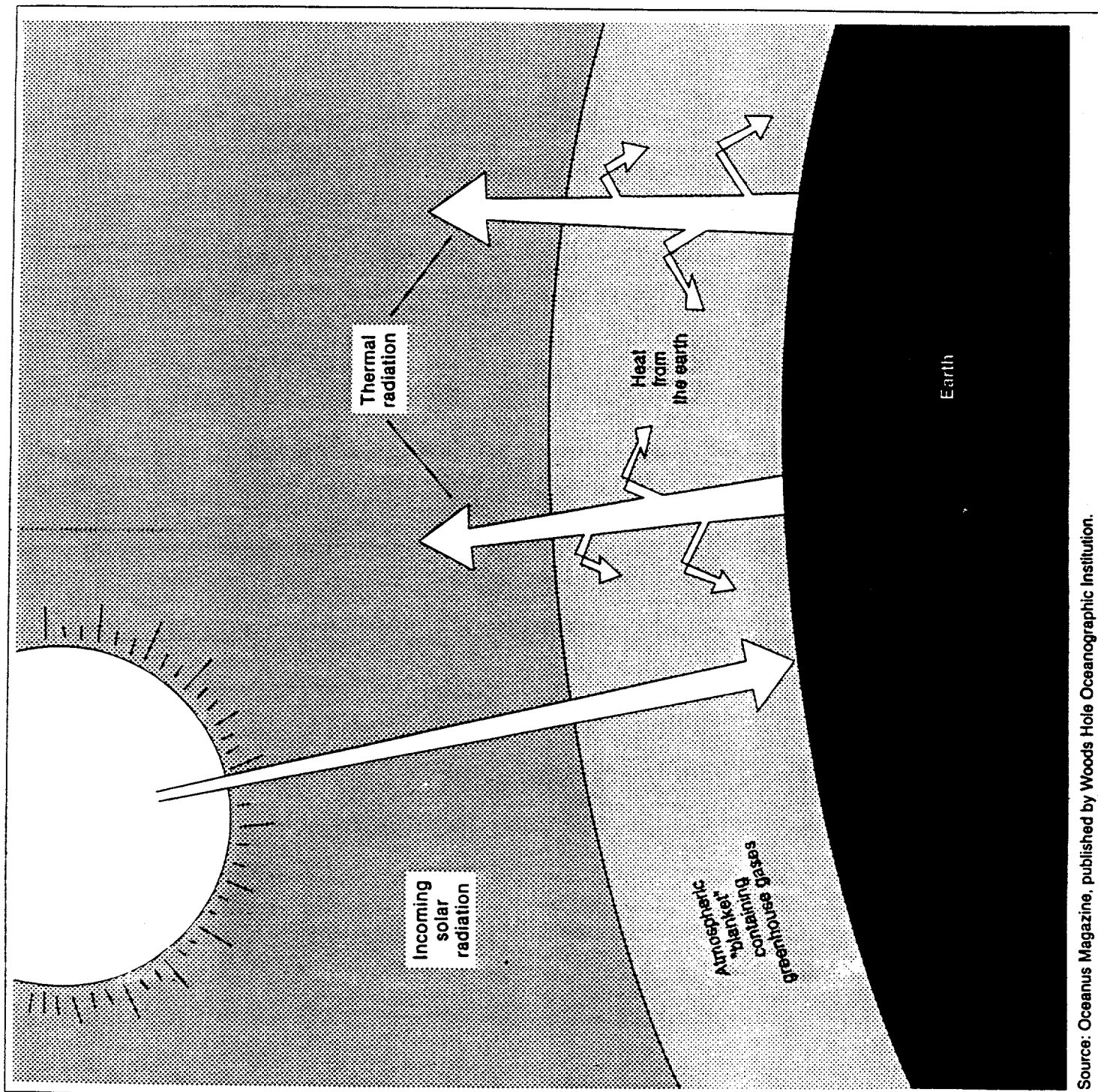


# **COPING WITH CLIMATE CHANGE: IMPLICATIONS FOR ENERGY CONSUMPTION**

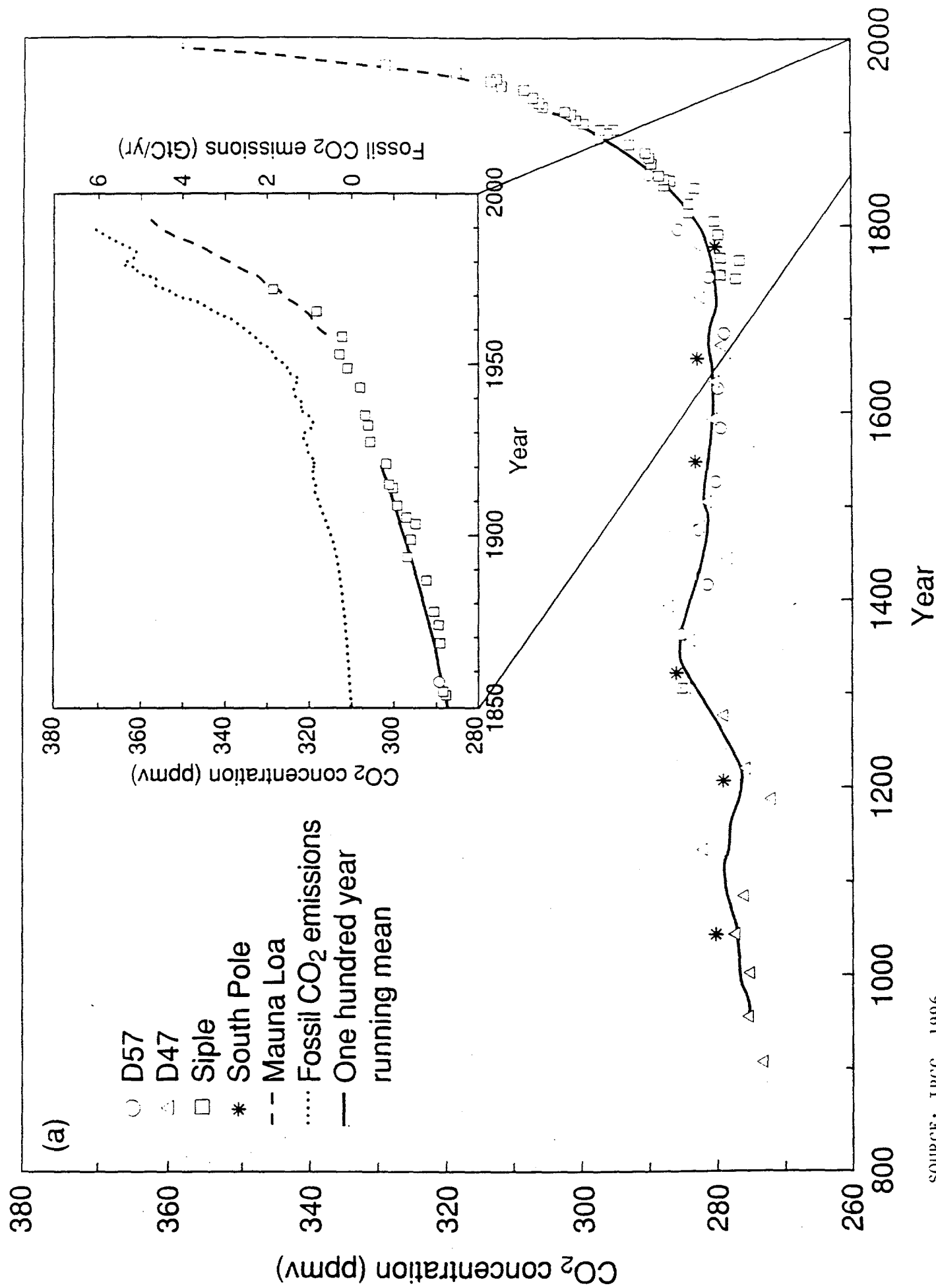
- There is a natural Greenhouse Effect. Earth is 60 F warmer than without it.
- Humankind is increasing concentrations of GHG
- Carbon dioxide is principal GHG; the most important source is fossil fuel burning.
- Observed changes consistent with climate modeling
- Without major cuts, irreversible changes will occur
- Message: must move to non-fossil energy
- Only two options: renewables and fission
- In either case, hydrogen needed as a “carrier”



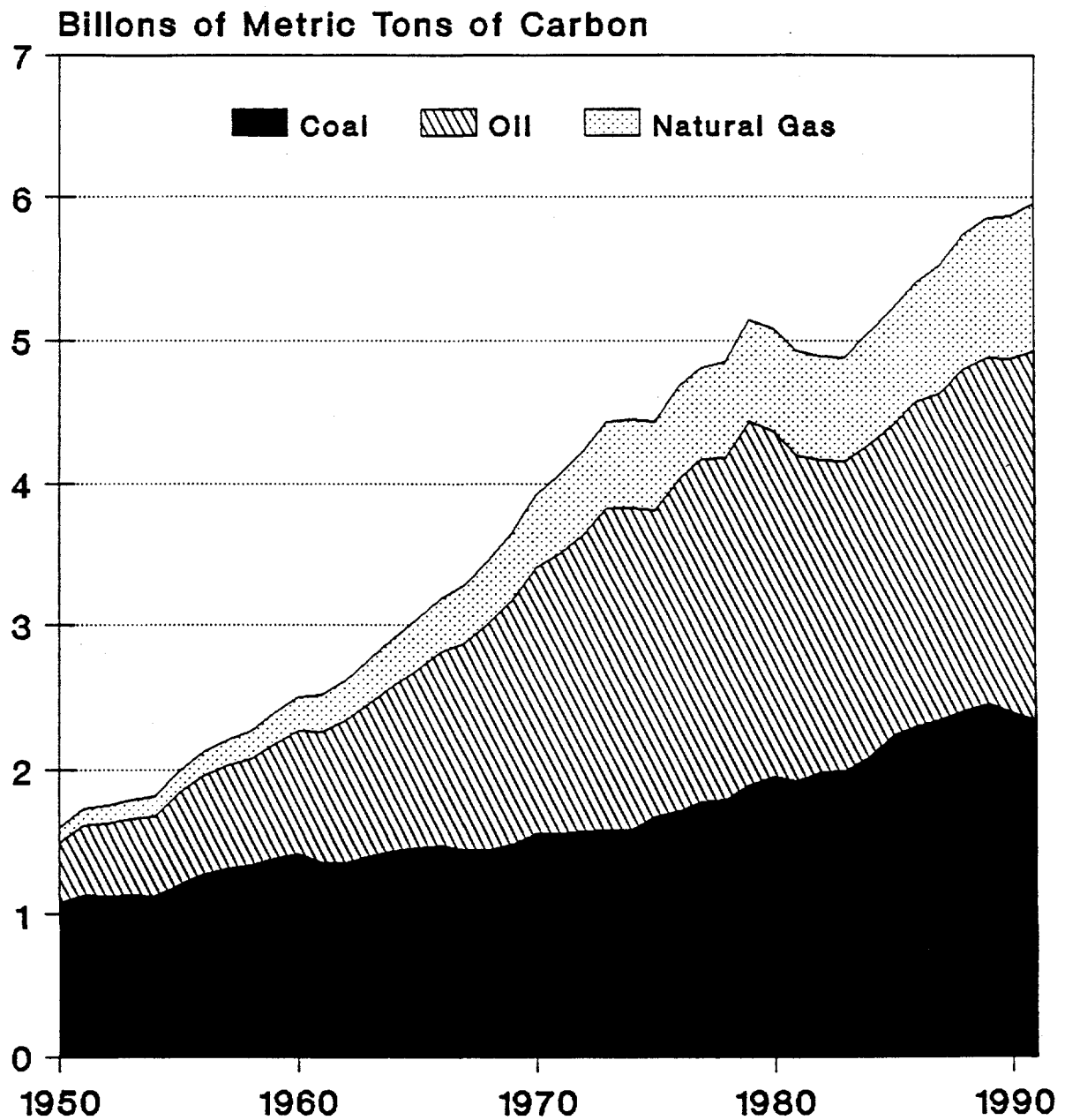
## The Greenhouse Effect



Source: Oceanus Magazine, published by Woods Hole Oceanographic Institution.

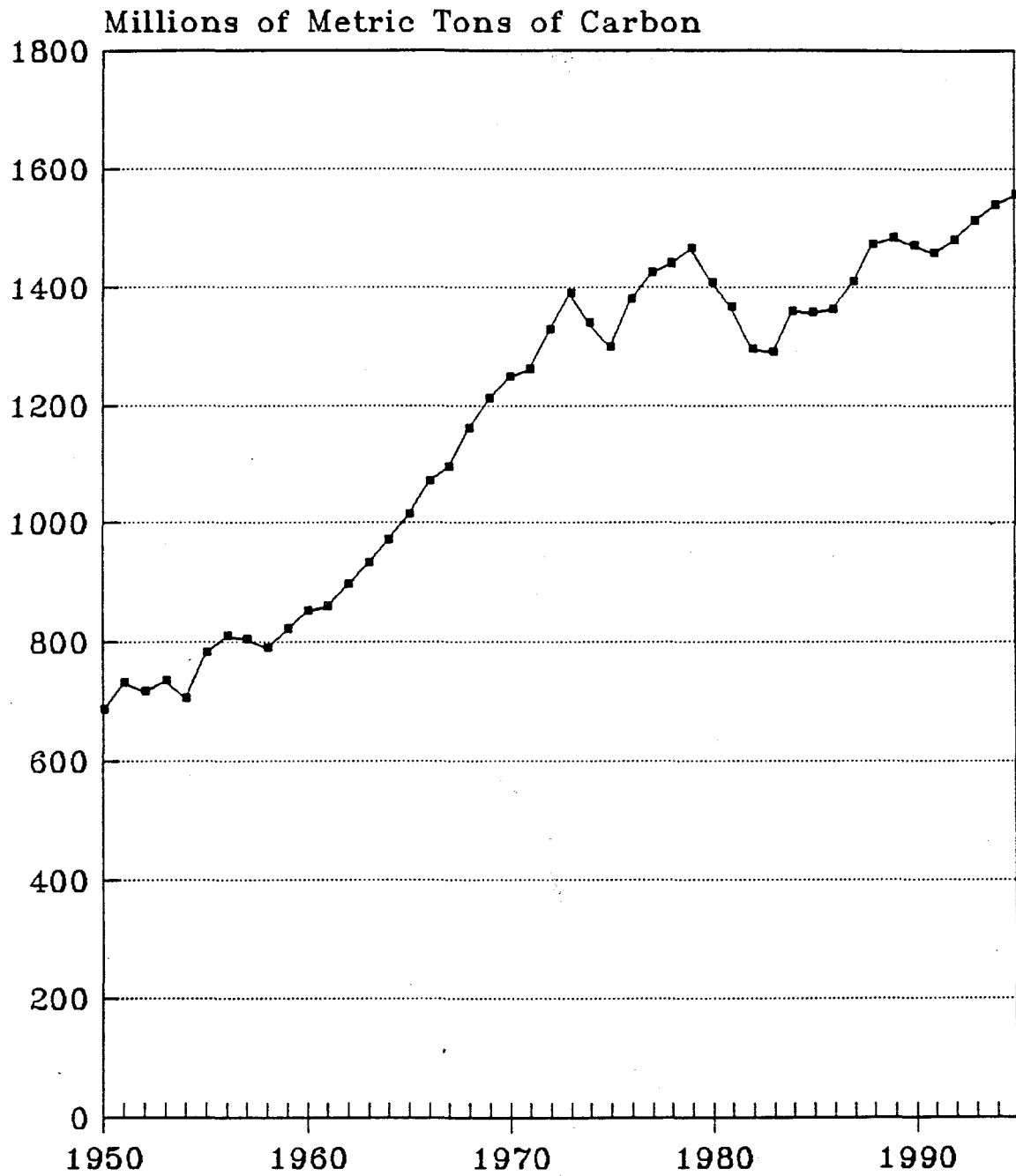


# GLOBAL FOSSIL-FUEL CARBON DIOXIDE EMISSIONS



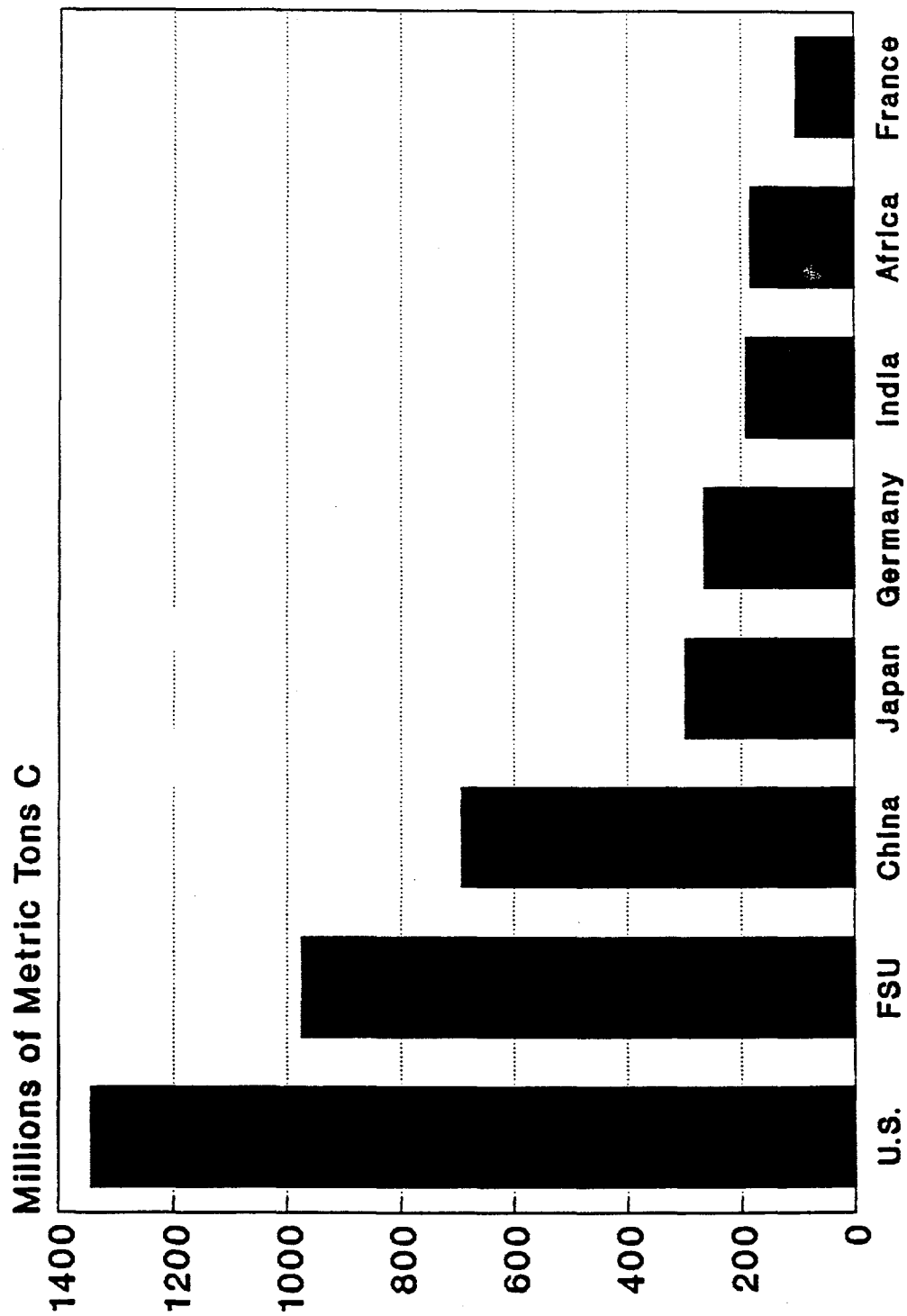
GLOCO2EM.2

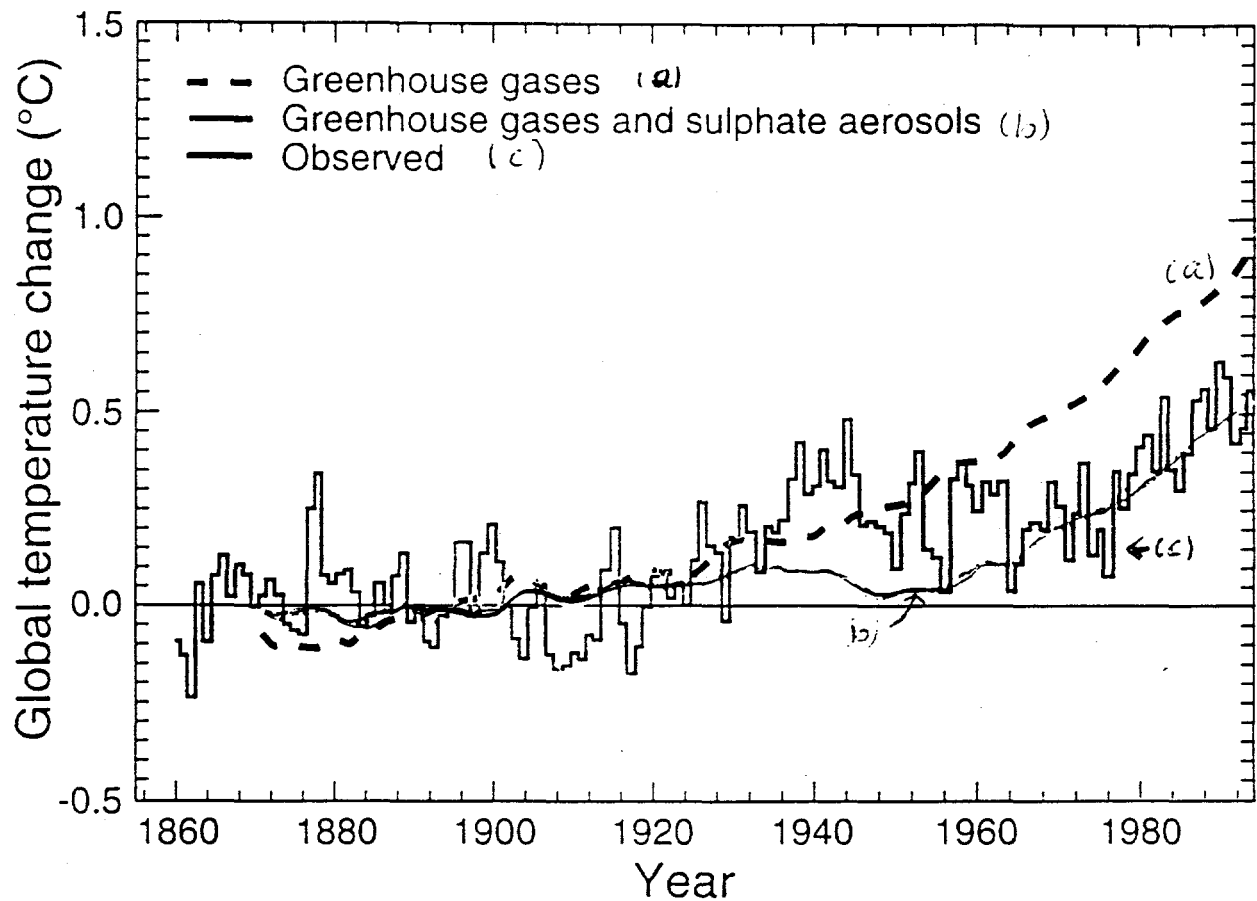
# U.S. CARBON DIOXIDE EMISSIONS



USCO2EMI.2

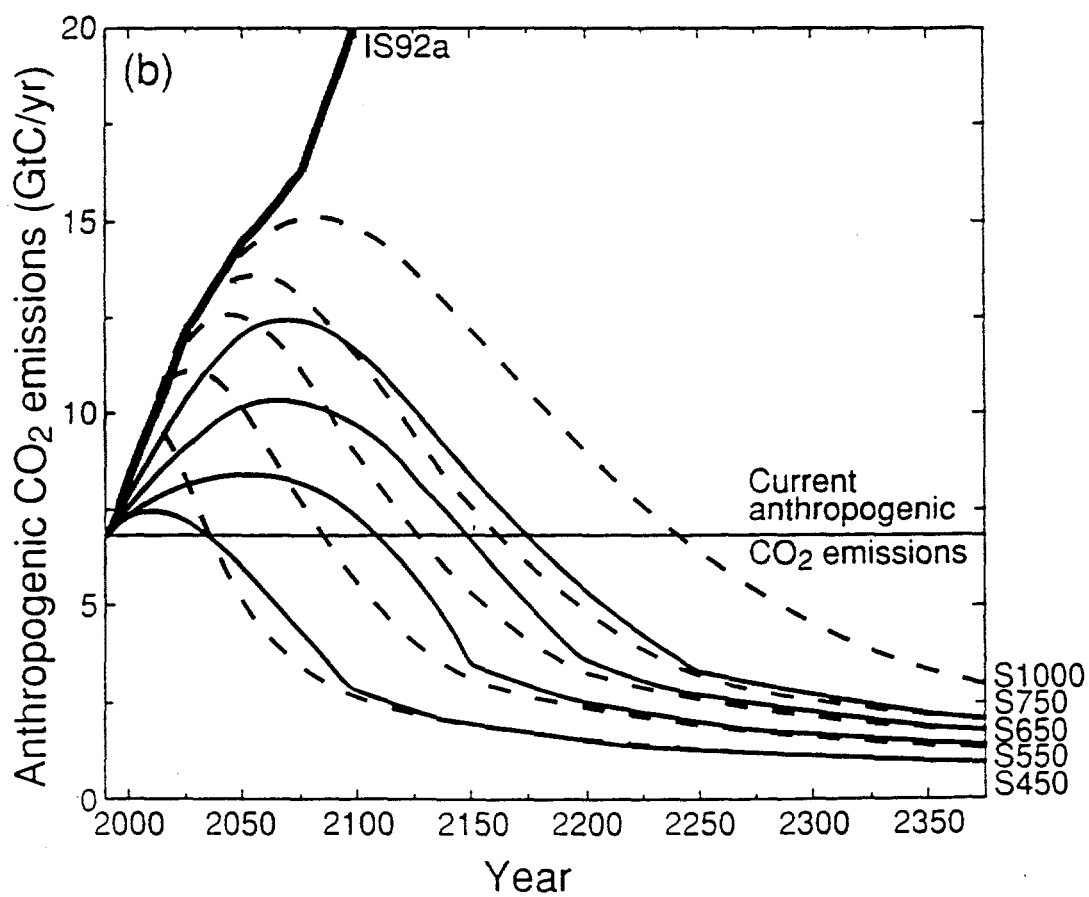
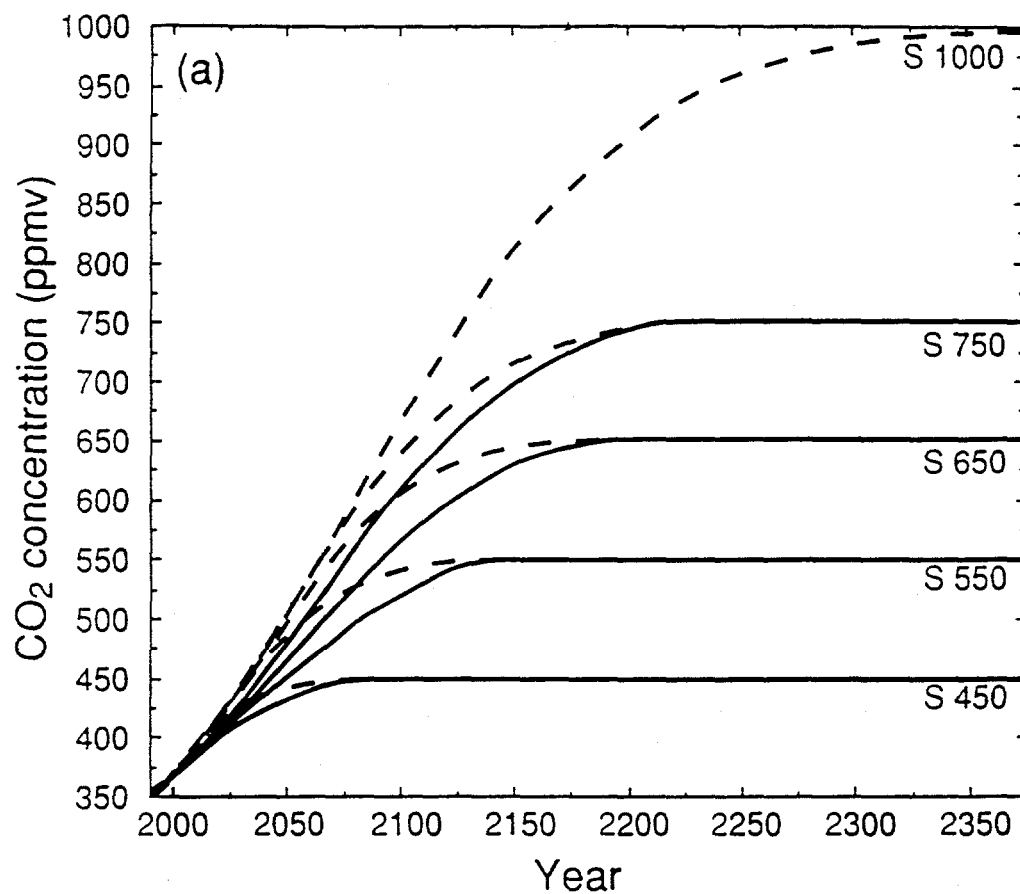
# CO2 EMISSIONS FROM FOSSIL FUELS FOR SELECTED REGIONS (1991)





*Simulated global annual mean warming from 1860 to 1990 allowing for increases in greenhouse gases only (dashed curve) and greenhouse gases and sulphate aerosols (solid curve), compared with observed changes over the same period.*

SOURCE: IPCC, 1995



# ***PROPERTIES OF RENEWABLE ENERGY TECHNOLOGIES***

- **ATMOSPHERIC FRIENDLY** (no carbon or pollutant emissions, except for biomass)
- **INTERMITTENT** (day and night, windy or calm, rain or drought, etc.)
- **DIFFUSE** (They require large collection areas)
- **MOSTLY ELECTRICITY SOURCES** (Except for biomass and water heaters)
- **UTILITY** of renewables improved with energy storage (hydrogen, batteries, flywheels)



## ***HYDROGEN RESEARCH NEEDS AND GOALS***

- Production -- Reduce costs and improve efficiency of renewably generated hydrogen
- Storage -- Reduce costs and weight; increase volume. Especially important in transportation applications
- Continue fuel cell improvements
- Explore hydrogen-based "total energy systems" for buildings
- Ensure that new technology is safe and "consumer friendly"
- Continue research on alternative infrastructures for introducing hydrogen

# Computer Modeling in the Design and Evaluation of Electric and Hybrid Vehicles

Salvador Aceves-Saborio<sup>1</sup>

J. Ray Smith<sup>1</sup>

Norman L. Johnson<sup>2</sup>

1. Lawrence Livermore National Laboratory

2. Los Alamos National Laboratory

## ABSTRACT

Modeling is an important tool in the design and evaluation of vehicles. Direct testing of vehicles is expensive, time-consuming and difficult. While it is recognized that vehicle testing is always necessary, models can provide accurate estimates of vehicle performance at reduced cost and effort. The current research and development activity on alternative-fuel vehicles is a result of stricter emission regulations and federal goals for high-efficiency automobiles. Therefore, the use of accurate engine and vehicular modeling tools, especially when applied to non-conventional cars and power trains continues to grow in importance.

The demonstration will begin with an overview of the use of engine and vehicle modeling tools. Next, the LLNL hybrid evaluation code will be applied to electric and hybrid vehicles, with an emphasis on the use of hydrogen as an ideal low-emissions fuel. Vehicle components may include: engines, fuel cells, batteries, flywheels, motors, and generators. A set of data files will be provided as examples. These files can be edited with a text editor to run different vehicle configurations. This demonstration is intended to serve two purposes: 1) illustrate the changes in performance and fuel economy that result from the changes in vehicle characteristics, and 2) show the application of simulation tools to solve current engineering problems.

# Computer Modeling in the Design and Evaluation of Electric and Hybrid Vehicles

Salvador M. Aceves<sup>1</sup>, J. Ray Smith<sup>1</sup>, and Norman L. Johnson<sup>2</sup>

<sup>1</sup> Lawrence Livermore National Laboratory

<sup>2</sup> Los Alamos National Laboratory

**Key Words:** Hybrid vehicles, Electric vehicles, Hydrogen fuel, Vehicle simulation.

**Prerequisite Knowledge:** Computer science (executing a Fortran program), analysis techniques (plotting numerical results, comparison of simulation runs), vehicle design (some knowledge of components of automobiles).

**Objectives:** To illustrate the changes in performance and fuel economy that result from the changes in vehicle characteristics, and to show the application of simulation tools to solve current engineering design problems.

**Supplies:** Computer with Fortran compiler, text editor, graphics plotting software. Modeling code is available from nlj@lanl.gov

## Introduction:

Light-duty vehicles (consumer automobiles), are major contributors to urban air pollution and greenhouse emissions. They also consume much of the oil supply to the country, causing oil dependence on unreliable foreign sources.

This demonstration project uses modern simulation techniques to illustrate the important technologies and design variables that an auto-designer would consider in producing a high efficiency, low emissions vehicle. Simulation and modeling techniques use the idea capturing the relationships between real components of the system with mathematical equations. These equations are then solved on a computer to simulate the behavior or performance of the system under various conditions. Simulations and models are a useful analysis tool for the following reasons:

- To provide insight and understanding of the real system  
Especially the complex dynamics from the interaction of simple physics
- To predict the performance, given modifications of the system.
- To supplement experimental results  
Especially when experiments are costly, unavailable or of low fidelity.
- To optimize the performance of the system.
- To develop control or operation strategies of the system.

In the current demonstration project, we focus on many variations of a hydrogen-powered vehicle. The fuel that powers the vehicle is hydrogen gas. When hydrogen is burned in the presence of an excess of oxygen (a lean mixture), the only combustion product is water. There is carbon monoxide (CO), a poisonous gas; or carbon dioxide (CO<sub>2</sub>) an undesirable greenhouse gas, produced, ; and very little nitric or nitrous oxides (NO and NO<sub>2</sub>), pollutants that cause brown hazes and are very irritating to the lungs.

Furthermore, hydrogen can be produced from renewable sources, such as solar or wind power, thereby eliminating our dependence on oil in the US and on foreign oil. Even

## *Computer Modeling in The Design & Evaluation of Electric and Hybrid Vehicles*

In the current demonstration project, we focus on many variations of a hydrogen-powered vehicle. The fuel that powers the vehicle is hydrogen gas. When hydrogen is burned in the presence of an excess of oxygen (a lean mixture), the only combustion product is water. There is almost no carbon monoxide (CO), a poisonous gas; or carbon dioxide (CO<sub>2</sub>) an undesirable greenhouse gas, produced; and very little nitric or nitrous oxides (NO and NO<sub>2</sub>), pollutants that cause brown hazes and are very irritating to the lungs. Furthermore, hydrogen can be produced from renewable sources, such as solar or wind power, thereby eliminating our dependence on oil in the US and on foreign oil. Even more exciting is that when used in a properly designed combustion engine or fuel cell, the power plant can achieve very high efficiencies, much higher than modern combustion engines used in automobiles.

The demonstration project also focuses on a particular type of vehicle, the series hybrid vehicle, that has been shown to have much higher operating efficiencies. When the high efficiency, low emission hydrogen engine is combined with a high efficiency series hybrid vehicle, the result is a vehicle that has nearly zero emissions, performs well, and is highly efficient.

### **The Series-Hybrid Vehicle with Advanced Energy Storage**

Series hybrid vehicles provide an alternative for obtaining vehicles with high fuel economy. Gasoline engines in conventional cars typically have a peak efficiency of approximately 32%. However, most of the driving is done with the engine operating at low power conditions, during idling or city driving. At low power conditions, the engine operates well below its optimal efficiency, resulting in a lower vehicle fuel economy. In a series hybrid vehicle the engine always operates at or near its optimum, without ever idling. The components of a series hybrid vehicle are shown in Figure 1. A critical difference between a conventional vehicle and a series hybrid vehicle is in the power train. This is shown schematically in Figure 2. Conventional cars have a direct mechanical link from the engine to the transmission and to the wheels, and therefore the engine operating conditions are set by the vehicle speed and power demands. Series hybrid vehicles do not have a mechanical link between the engine and the wheels; an electric motor provides the tractive power and recovery of energy during braking (called regenerative braking). The engine can be an internal combustion engine (abbreviated ICE), as found in current automobiles or fuel cells, the power plants of the future.

An engine in a series hybrid vehicle operates in an on-off mode. When the engine is running it drives a generator that supplies electricity to both the electric motor and an energy storage system. Batteries or flywheels can be used for energy storage. The storage system supplies electricity to the traction motor when the engine is turned off. Because the storage system uncouples the engine from the wheels, electric power generation is at optimum efficiency. Series hybrid vehicles have a high fuel economy because the engine is both sized closer to the car's average power consumption and operated under its most efficient conditions without idling. As will be shown in this demonstration, series hybrid vehicles are very sensitive to the efficiency of the energy storage system, and consequently, an efficient energy storage system is necessary for obtaining a high fuel

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### **HVEC: The Hybrid Vehicle Evaluation Code:**

This demonstration illustrates the application of the Hybrid Vehicle Evaluation Code (HVEC) to hydrogen hybrid vehicles. The analysis describes the operation of series hybrid vehicles, and the sensitivity of vehicle fuel economy to some of the main vehicle parameters. HVEC can be used to analyze all electric vehicles and hydrogen-fueled hybrid vehicles. Vehicle components may include: combustion engine, fuel cell, battery, flywheel, motor, and generator. The present demonstration concentrates on series hybrid vehicles with hydrogen as a fuel, because these have the potential of reaching a very high fuel economy and near-zero emissions.

HVEC is a Fortran computer code that models the performance and emissions of an all electric or hybrid vehicle in response to a variety of operating conditions. The physics

included in the code are simple dynamics - a certain amount of energy is required to perform a specified task. The model includes relationships between operating conditions and required performance data, such as various energy losses in the system or emissions. These relationships are obtained from a variety of sources: experimental, more complex computer simulations, or analytical studies. HVEC is one of a broad class of simulation codes that help designers quickly analyze the performance of a system given a variety of competing designs or operating conditions. The results are then used to select the optimal design, to focus on areas of needed improvement, to optimize the operating conditions, or to gain insight into the dynamics of the system. This broad class of simulation codes are called thermodynamic, zero-dimensional, or system simulation codes, and they offer rapid solutions that are accurate within the applicability of the correlations used in the code. Other simulation codes are used to examine more details of the operation of components of the larger system, like the operation of the hydrogen-fueled engine or the flywheel. These "multi-dimensional" codes require fewer assumptions about the dynamics of the system and are often used to provide the system simulation codes with the necessary correlations. An example of these is KIVA, a code developed at Los Alamos National Laboratory for analysis of fluid mechanics and combustion phenomena inside an internal combustion engine [1].

The sequence of processing in the HVEC code is (1) reading the input files that define the vehicle and the performance characteristics of the components, (2) evaluating the performance of the vehicle under specified driving schedules, and (3) producing a list of the results. HVEC runs in non-interactive mode, with all the vehicle and component parameters specified in data files, which can be modified with a text editor. The data file that specifies the hydrogen series hybrid vehicle is titled "4HYBFLY.CAR." This needs to be modified for this demonstration. Other data files used in the program that do not need to be modified are: driving schedule, battery, fuel cell, and motor files (extension names .SCH, .BTR, .FCL, and .MOT). The results of the execution of the program are in data files that have an extension name .DAT. HVEC does not provide a graphic post processor, but the .DAT files can easily be imported in a graphing package.

### **Procedure for using HVEC :**

Start by using a text editor to see the contents of the 4HYBFLY.CAR file. The file contains data for a specific hybrid concept vehicle that has been developed at Lawrence Livermore National Laboratory over the last few years [2,3]. The most important vehicle parameters are listed in Table 1 and in Figure 1. Exit the text editor without modifying the data file, and execute HVEC. When called, the program responds with a list of 8 vehicle configurations that can be analyzed. Choose "engine-flywheel hybrid" by typing 4 followed by the Enter or Return key. The program asks for the names of the vehicle file, and two results files. Press Enter three times to accept the default names (4HYBFLY.CAR, RESULTS.DAT, and SUMMARY.DAT). The program first calculates fuel economy and emissions by running a simulated drive of the concept vehicle over two driving cycles: the urban and highway driving cycles specified in the EPA Federal Test Procedure. Results for the urban and highway cycles are then used for calculating results for the combined cycle. The combined driving cycle is defined as 55% urban driving and 45% highway driving. After finishing the simulated drives, HVEC calculates vehicle acceleration performance (time for 0-97 km/h, 60 mph), and hill climbing performance (hill slope in % that the car can climb at a constant 97 km/h, 60 mph). When the program is finished, use the text editor to read the results from the SUMMARY.DAT file. The most important results are listed at the end of the file, and included here in Table 1.

The results in Table 1 indicate that the vehicle has a very high fuel economy, approaching the 80 mpg goal set by the Federal Government through the Partnership for a New Generation of Vehicles. Vehicle engine and motor are specified to meet performance parameters considered acceptable for the general public (6% hill climbing at 97 km/h and 10 seconds for 0-97 km/h acceleration).

Next, the file FLYWHEEL.DAT can be used to illustrate series hybrid vehicle operation. Import the file into a graphics software, and make a plot of the fourth column (state of charge) in the y-axis, vs. the first column (time) in the x axis. Only the results for the urban cycle need to be plotted. Results for the highway cycle follow those for the urban cycle in the file. These can be deleted before making the plot. Figure 3 shows the results. This figure shows flywheel energy storage divided by its maximum capacity as a function of time. Initially, the state of charge is low and the engine is running to charge the flywheel. When the flywheel is charged (at about 130 seconds), the engine is turned off, and the flywheel provides all the energy for accessories and transportation. When the flywheel is discharged again, the engine is turned on to repeat the cycle.

Finally, HVEC is applied to analyze the sensitivity of vehicle fuel economy (combined cycle) to the following vehicle parameters: test weight, frontal area, rolling friction coefficient, flywheel efficiency, and accessory load. This is to determine which of these parameters has the greatest effect on fuel economy, indicating where the greatest efforts should be directed for obtaining high fuel economy vehicles. To do this, start by multiplying the test weight by 0.9 ( $1272 \times 0.9 = 1145$ ) and substitute the result as the test weight in the file 4HYBFLY.CAR. Run HVEC and obtain the combined cycle fuel economy from the SUMMARY.DAT file (this can also be read directly from the screen). The result is 33.7 km/l (79.2 mpg). Now, change the vehicle weight in the data file back to its original value, and replace the value of the frontal area by 90% of its original value and run HVEC. Repeat this procedure for all the variables listed above, keeping all variables at their original value, except for the single variable being modified. The fuel economy obtained from these runs can then be used in obtaining the percent change in fuel economy that results from a 10% reduction in any vehicle parameter. The percent change in fuel economy for a 10% change in vehicle weight is:

$$100 \times (79.2 - 75.6) / 79.2 = 4.54\%$$

All other percent changes are calculated in a similar way. The results are illustrated in Figure 4. The figure shows the percent change in vehicle fuel economy for a 10% reduction in the given parameters. The percent change in fuel economy due to reductions in mass, area, rolling friction coefficient, and accessories is positive because fuel economy increases when these parameters are reduced. Fuel economy decreases due to reductions in flywheel and engine efficiencies, resulting in negative changes for these variables. It can be seen that fuel economy is most sensitive to engine efficiency and flywheel efficiency (about 10% for a 10% change in these parameters), with smaller changes in fuel economy due to changes in weight, area, rolling friction coefficient, and accessories. The great sensitivity of fuel economy to flywheel efficiency is what makes it necessary to have an efficient energy storage system for series hybrid vehicles to be successful. A typical battery has an efficiency of the order of 70%, which may result in a low vehicle fuel economy. Accessories can increase substantially (up to 3 kW) if air conditioning or heating is required. Under these conditions, accessories would have a great effect on fuel economy.

**Suggestions for additional studies:**

1. Because the weight of the vehicle is included into HVEC, the importance of using advanced light-weight materials in the construction of the vehicle can be evaluated or the effect of using the vehicle as a light duty truck.
2. Suppose that fuel economy was less important than acceleration. Redo the above study looking at acceleration times.
3. The relative effect of changing the variables (such as the conclusion that the best payoff is to focus development in the proposed study is in the flywheel and engine design) differ under either various designs and operating conditions. Repeat the above study with a different design.
4. Use HVEC to optimize the vehicle transmission. Modify the value of the 1<sup>st</sup> gear reduction ratio given in the 4HYBFLY.CAR file (numbered 24). Make 11 runs of HVEC for values of the reduction ratio between 200 and 400 at intervals of 20, and keep a record of how the fuel economy changes as the gear ratio changes. A gear ratio will exist for which a maximum fuel economy is obtained. Also, keep track of the acceleration time as these runs are made. Minimum acceleration time (maximum vehicle performance) will not be obtained at the same gear ratio as maximum fuel economy. This is an example of conflicting requirements in vehicle design where a compromise has to be made between optimum performance and optimum fuel economy.

#### **Notes to the Instructor:**

1. When modifying the data files, make sure that no additional lines are introduced in the file. The file is read line by line, and if the required information is not found in the exact line, the program may crash or give wrong results. It is recommended that the original files be backed up before modifying to be able to recover from these problems.
2. Make sure to use an ASCII text editor. If a word processor is used, make sure that the files are saved as ASCII text.

#### **References:**

1. Amsden, A.A., 1993, "KIVA-3: A KIVA Program with Block-Structured Mesh for Complex Geometries," Los Alamos National Laboratory Report LA-12503-MS.
2. Smith, J.R., 1993, "The Hydrogen Hybrid Option." Proceedings of the Workshop on Advanced Components for Electric and Hybrid Electric Vehicles, Gaithersburg, MD, NIST special publication 860.
3. Aceves, S. M., and J. R. Smith, 1995, "A Hybrid Vehicle Evaluation Code and Its Application to Vehicle Design," SAE paper 950491.

#### **Glossary:**

**Accessories:** Automotive components that are necessary for meeting passenger needs not directly related to transportation. Accessories include air conditioner, radio, powered windows, etc.

**Accessory load:** Power required to drive all accessories, in Watts. Air conditioning and heating are the accessories that require the most power.

**ASCII:** Format for storing information in a computer. This format only permits the use of 256 basic characters. This is a basic format that can be read and used in any computer.



Drag: Force exerted on a body as a result of the motion of a fluid around it. For cars, drag is given by the following equation:

$$F_d = \frac{1}{2} C_d \rho A v^2$$

where  $C_d$  is the drag coefficient,  $\rho$  is the air density,  $A$  is the vehicle frontal area, and  $v$  is the velocity.

Drag coefficient: Constant used in calculating drag. See above.

Flywheel: A rotating mass used to store kinetic energy. A flywheel stores energy as its speed increases, and gives up energy as its speed decreases. Advanced flywheels rotate at speeds of up to 80000 revolutions per minute.

Fuel cell: Device that converts fuels into electrical energy through electrochemical rather than mechanical means.

Partnership for a New Generation of Vehicles: A collaboration between the Federal Government and the car manufacturers (Ford, GM, and Chrysler) to develop high fuel economy, low emitting vehicles.

Regenerative braking: Braking in which the loss of kinetic energy from braking is stored and subsequently fed back to provide tractive effort. Currently it is only practical in electric and series hybrid vehicles where braking can be achieved by using the motor as a generator.

Rolling friction: Retarding effect on a vehicle, consisting primarily of tire and mechanical friction. It is calculated as:

$$F_r = r m g$$

where  $r$  is the rolling friction coefficient,  $m$  is the vehicle test weight, and  $g$  is the acceleration of gravity ( $9.8 \text{ m/s}^2$ ).

Tractive power: Power required to move a car under a given set of conditions.

Table 1. Main parameters and results (fuel economy and performance) for the LLNL concept hydrogen hybrid vehicle specified in 4HYBFLY.CAR.

Vehicle parameter	Value
Test weight, kg (empty weight +136 kg)	1272
Frontal area, m <sup>2</sup>	2.04
Drag coefficient	0.24
Rolling friction coefficient	0.007
Flywheel turnaround efficiency, %	90
Accessory load, Watts	1000
Engine peak efficiency, %	46
Generator peak efficiency, %	95
<b>Results</b>	<b>Value</b>
Fuel economy, urban driving cycle, km/l (mpg)	29.3 (69.0)
Fuel economy, highway driving cycle, km/l (mpg)	36.4 (85.6)
Fuel economy, combined driving cycle, km/l (mpg)	32.1 (75.6)
Time to reach 97 km/h (60 mph), seconds	10.0
Climbing slope at 97 km/h (60 mph), %	5.96

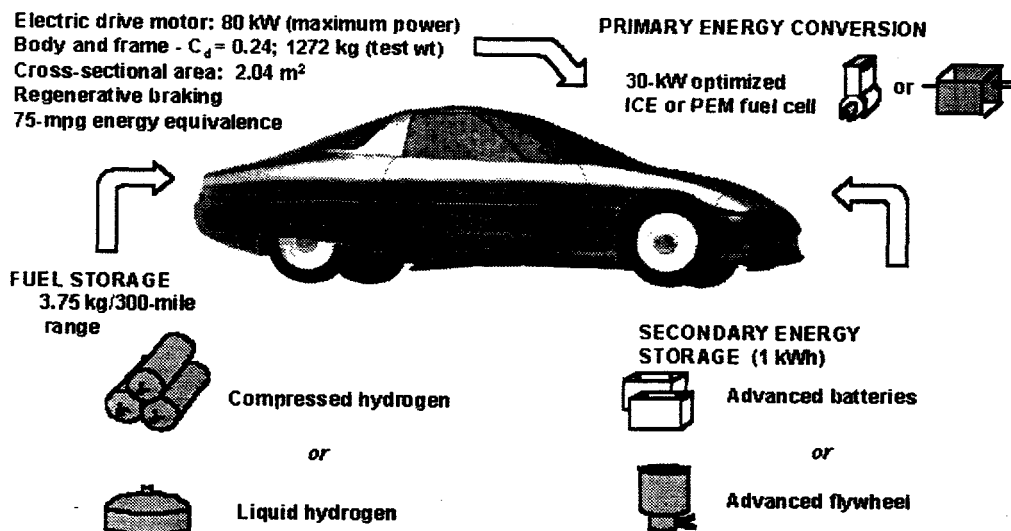
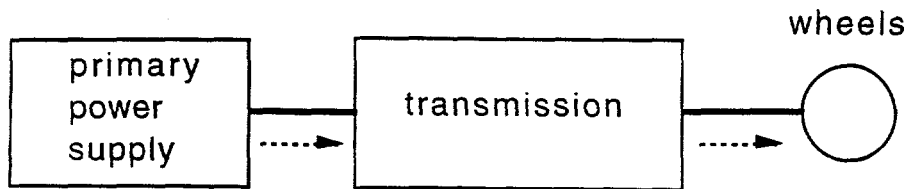
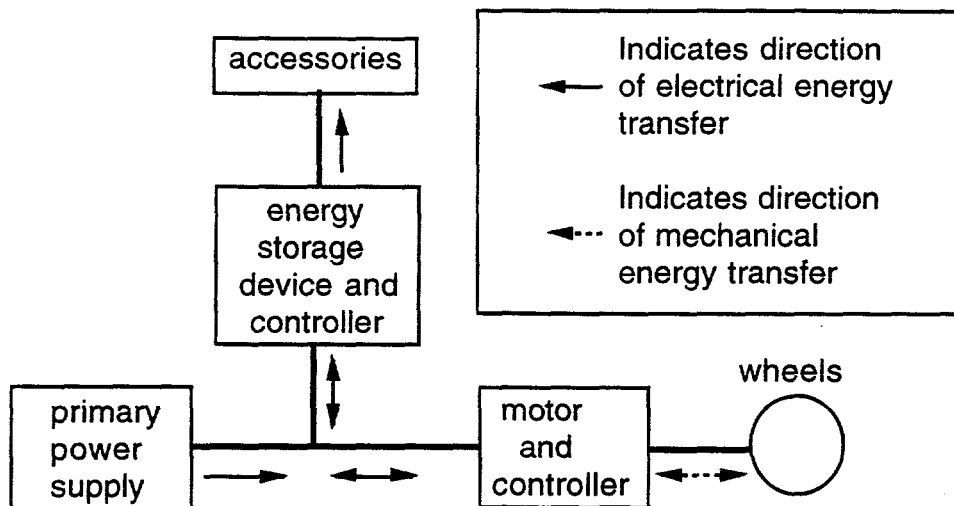


Figure 1. Components of a hydrogen series hybrid vehicle, including engine, fuel storage and energy storage device.



(a) conventional vehicle power train



(b) series hybrid power train

Figure 2. Schematic of a conventional car and a series hybrid vehicle power train. For the series hybrid vehicle described in this demonstration, the primary power supply is a hydrogen engine, and the energy storage device is a flywheel.

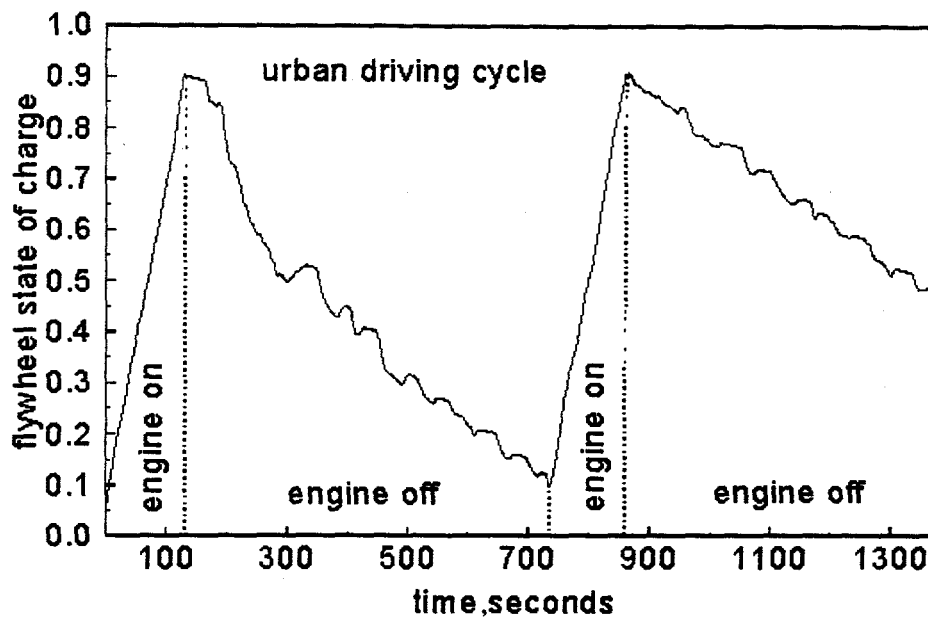


Figure 3. Flywheel state of charge (energy stored in the flywheel divided by the maximum energy that can be stored in the flywheel) as a function of time, for the hydrogen hybrid concept vehicle during the urban driving cycle.

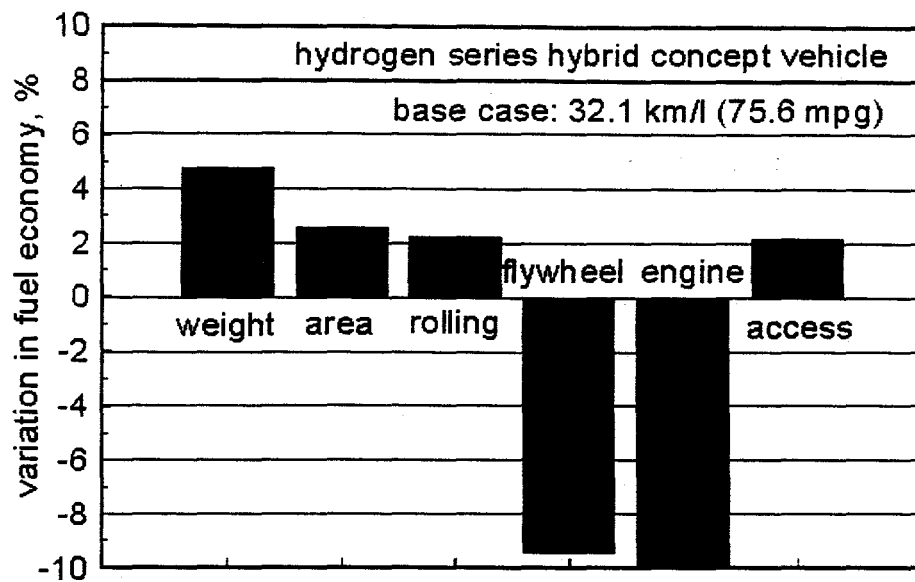


Figure 4. Percent change in vehicle fuel economy for a 10% reduction in the given parameters. The labels in the column represent the following vehicle parameters: weight is the test weight; area is the frontal area; rolling is the rolling friction coefficient; flywheel is the flywheel turnaround efficiency; engine is the engine efficiency; and access is the accessory load.

## **Light-Duty Vehicles (consumer automobiles)**

---



- Major contributors to urban air pollution (hydrocarbons, carbon monoxide, nitrous oxide)
- Major producers of greenhouse gases (carbon dioxide)
- Consume much of the oil supply, causing oil dependence on unreliable foreign sources

# Hydrogen Fuel

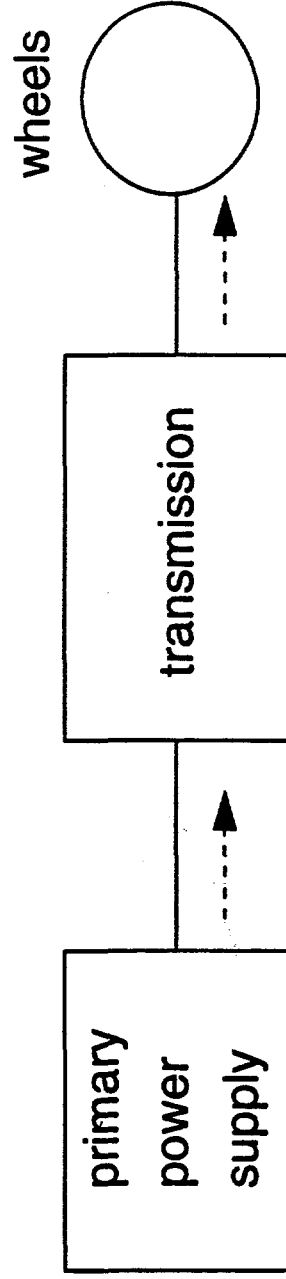
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- Clean fuel in either an engine or a fuel cell (very low hydrocarbons, carbon monoxide or nitrous oxide).
- High efficiency in engines and in fuel cells.
- Potentially renewable, obtained from
  - solar energy
  - wind energy
- without depleting oil reserves

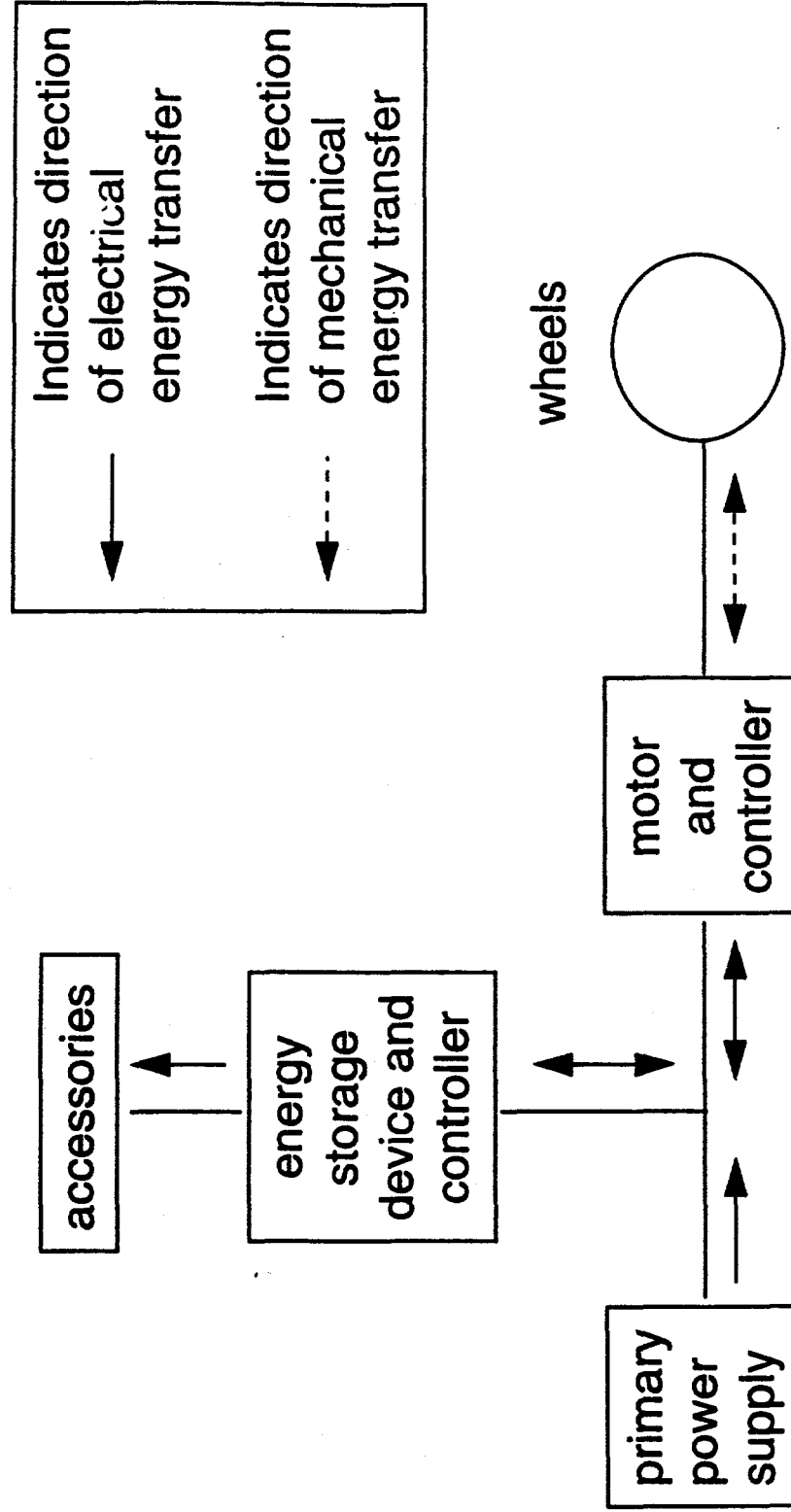


# Conventional Vehicle Power Train

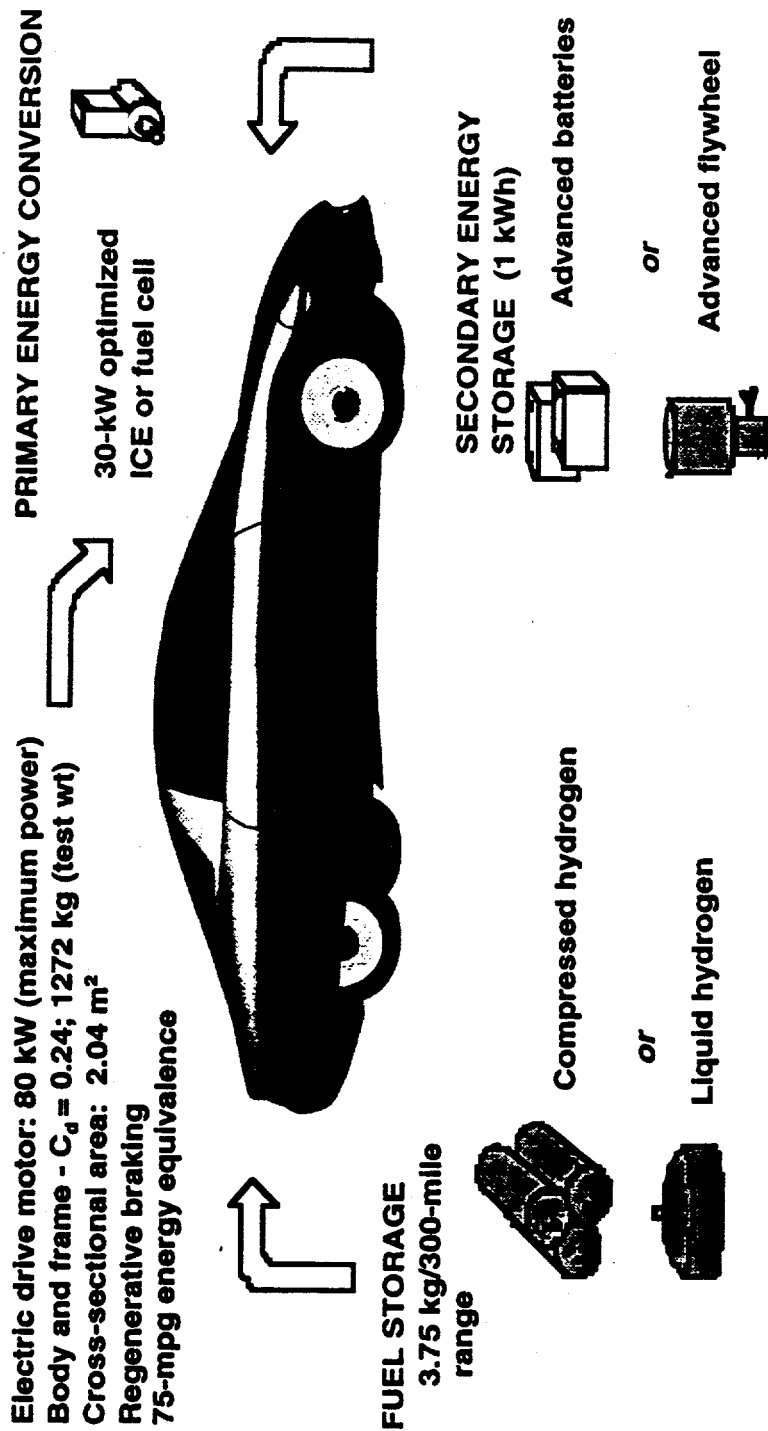


Indicates direction  
of mechanical  
energy transfer

# Series Hybrid Power Train



# Hydrogen Series Hybrid Vehicle



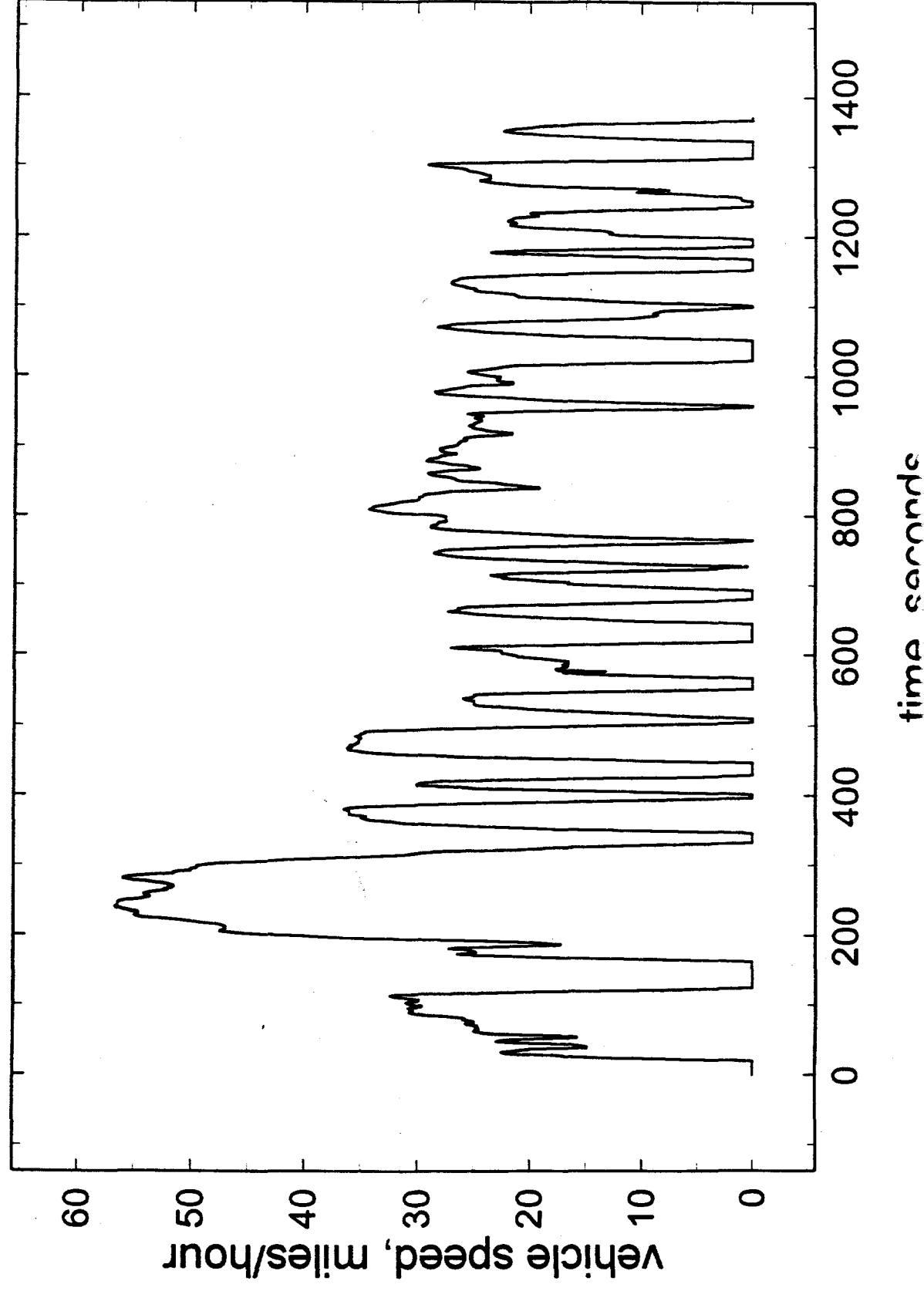
## **HVEC: The Hybrid Vehicle Evaluation Code**

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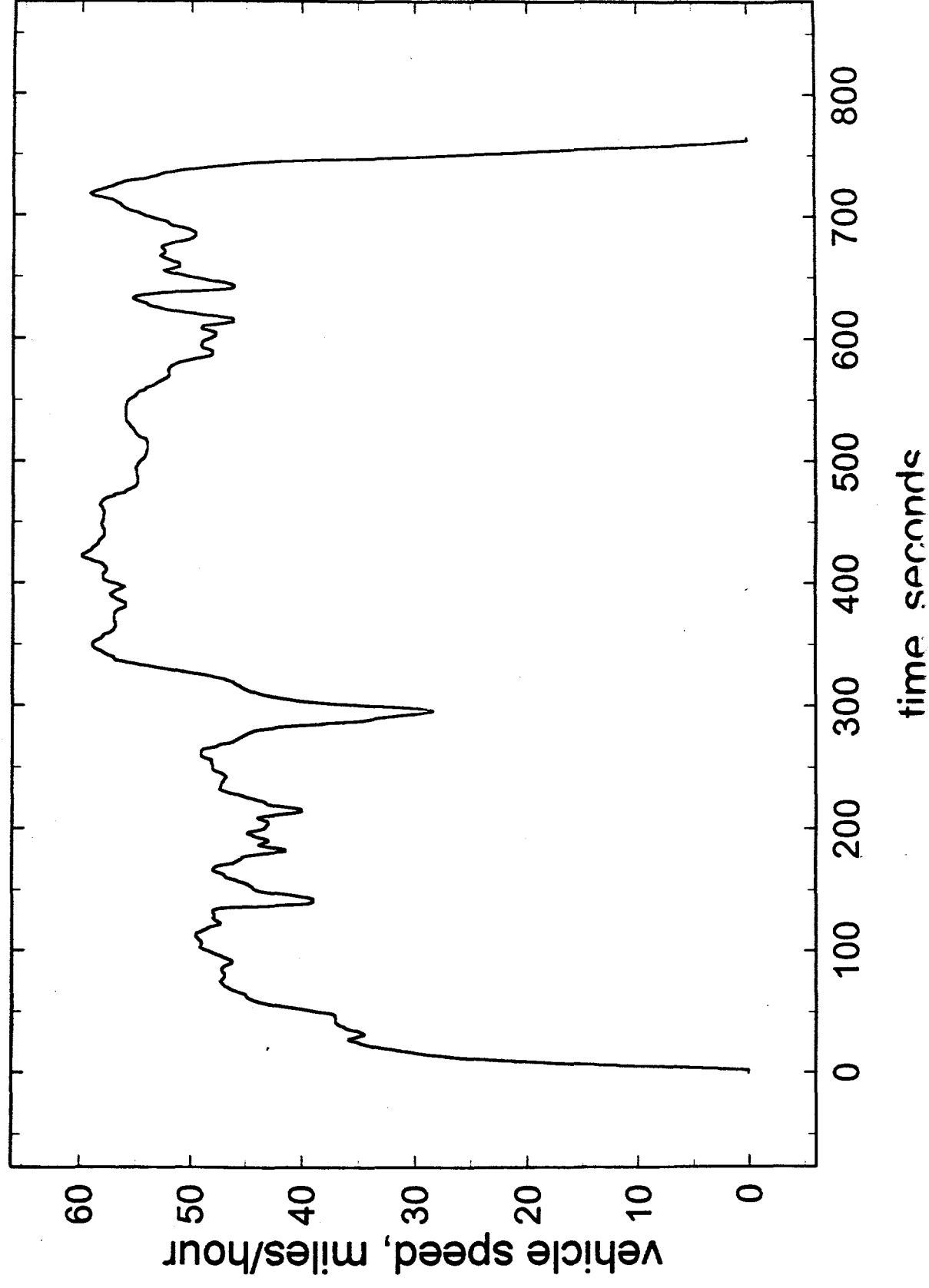


- Can analyze electric and series hybrid vehicles
- Can include any of the following vehicle components:
  - combustion engines
  - fuel cells
  - batteries
  - flywheels
  - motors
  - generators
  - transmissions

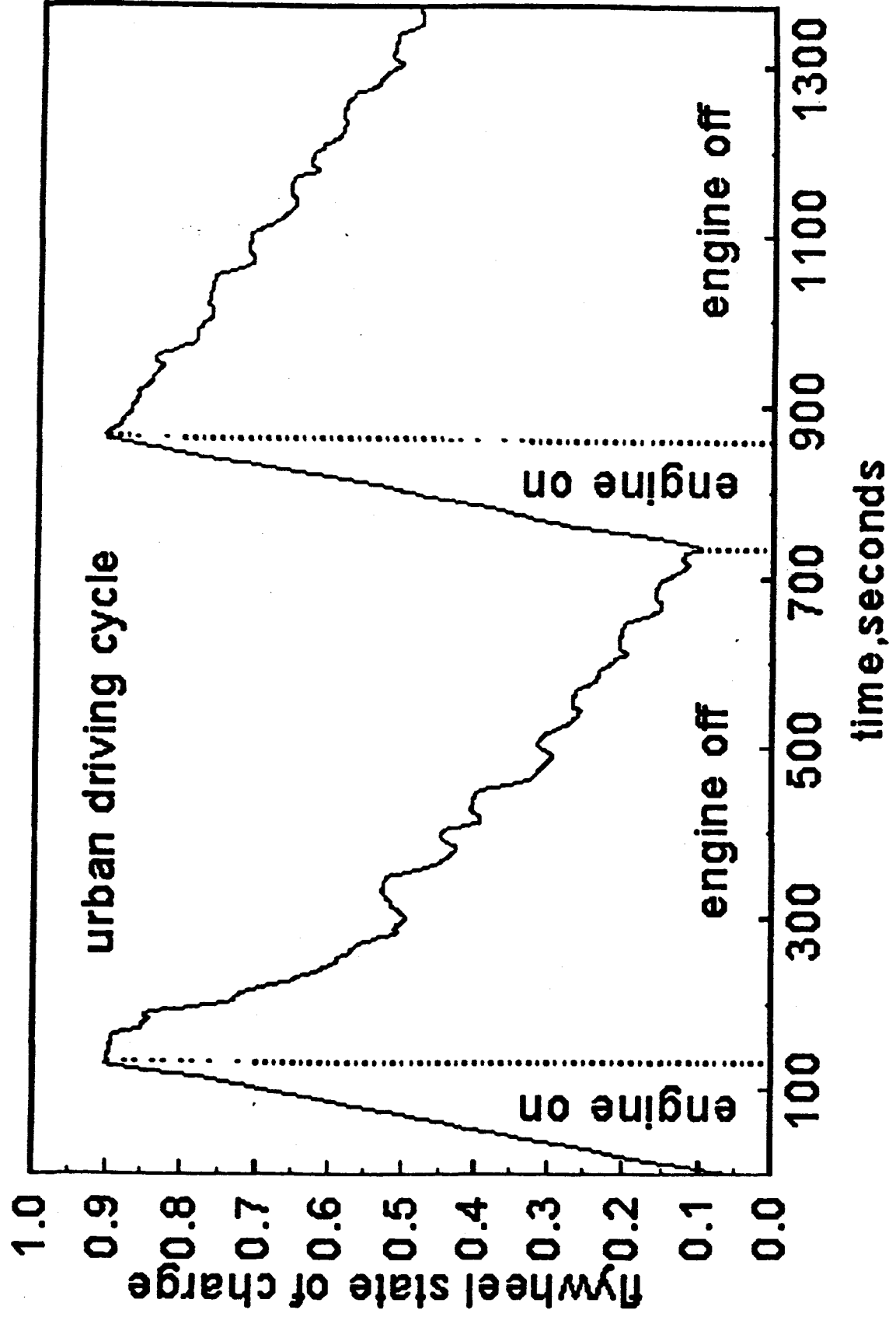
# HVEC simulates a drive through the urban driving cycle



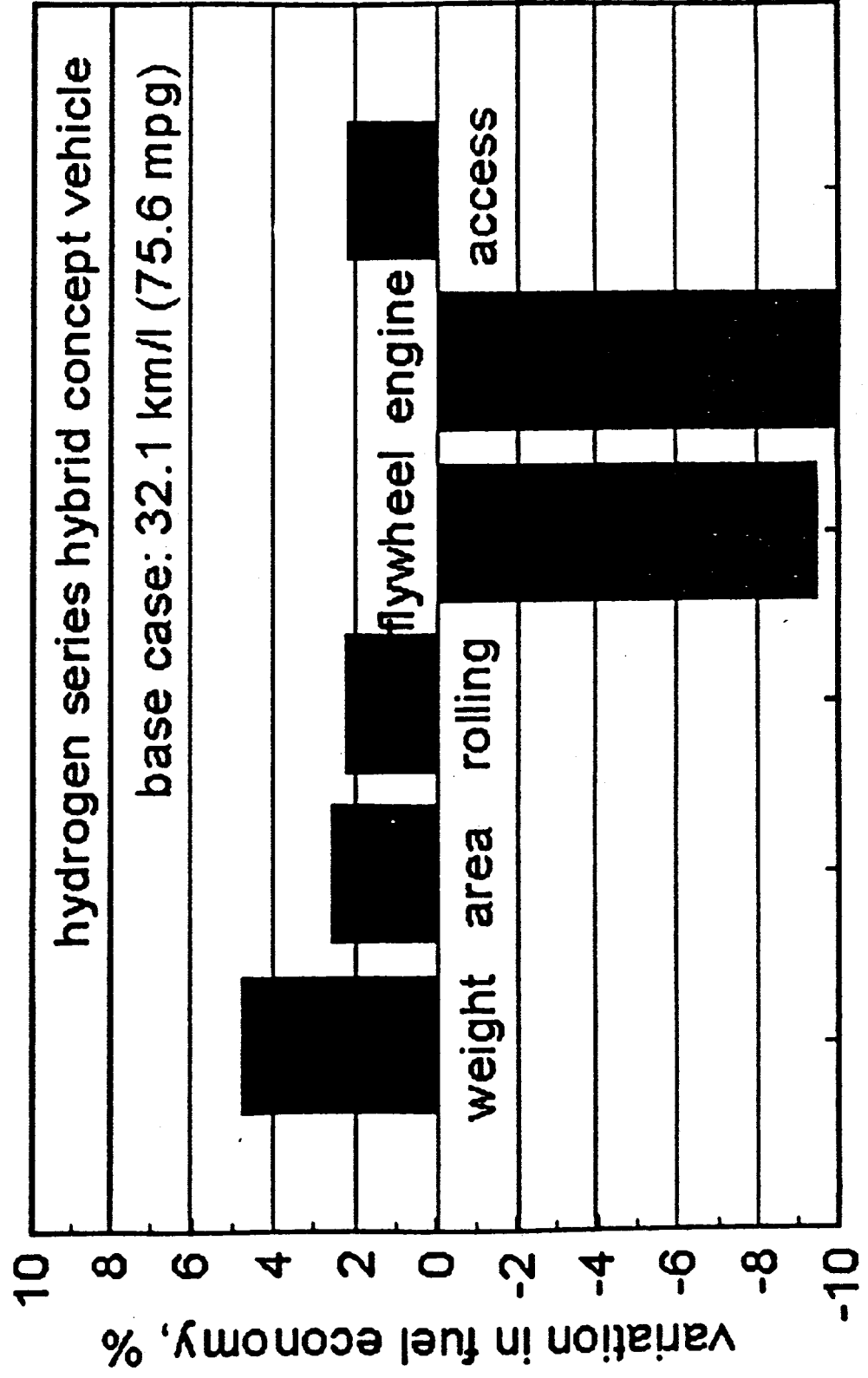
**The highway driving cycle is also used in HVEC**



## Series Hybrid Vehicle Operation Mode

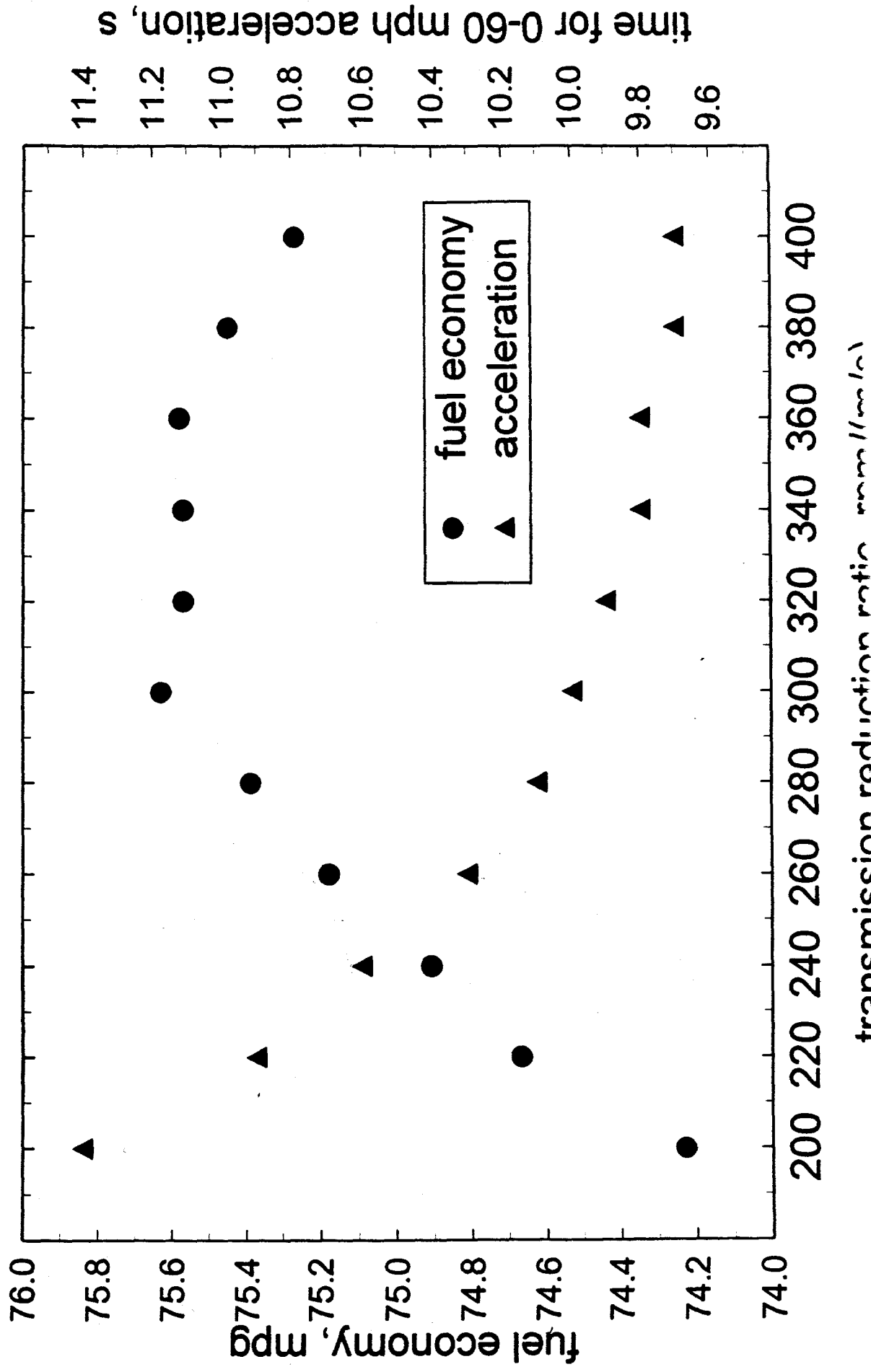


# Sensitivity Analysis for Series Hybrid Vehicle





## Additional study: Transmission Optimization



## EXPERIMENTS/DEMONSTRATIONS:

### EXPERIMENTAL INVESTIGATION OF HYDROGEN TRANSPORT THROUGH METALS

T.S. Moss and R.C. Dye  
Los Alamos National Laboratory  
Los Alamos, NM 87545

In this experiment, we shall examine the transport of hydrogen through different metals. The catalytic and transport properties of palladium will be compared and contrasted with the same properties of Group V metals. The fundamental differences in the way that hydrogen interacts with metals will be exploited to optimize the purification of hydrogen gas. This experiment demonstrates how a composite material can have better performance than the material's individual components. As a proof of this concept, the transport rate of hydrogen through a composite membrane to that of the constituent materials will be compared.

# EXPERIMENTAL INVESTIGATION OF HYDROGEN TRANSPORT THROUGH METALS

7-7328 7-3404  
Tom T.S. Moss and R.C. Dye Robert  
Los Alamos National Laboratory  
Los Alamos, NM 87545

**Key Words:** Hydrogen, transport, metals

**Prerequisite Knowledge:** Because hydrogen gas is used in this experiment, a working knowledge of *hydrogen safety is required*. Basic Material Science is helpful but not necessary.

**Objective:** To understand the fundamental differences in the way that hydrogen interacts with metals and to demonstrate how a composite material can have better performance than its individual components.

## Equipment:

1. Heat tape (350°C)
2. Thermocouple with readout
3. Variable power supply for the heat tape
4. 1/2 inch VCR® components: male and female (Metal pipe fittings from CAJON)
5. Palladium foil
6. Vanadium foil
7. Composite foil
8. Hydrogen gas
9. Beaker
10. Graduated cylinder
11. Tubing

## Introduction:

→ With the steady depletion of fossil fuel reserves, hydrogen based energy sources are becoming increasingly attractive. This is creating a continued and building interest in developing economically viable methods for hydrogen separation from additional sources such as natural gas and methanol reforming. Furthermore, such separation techniques can also be applied to the chemical industry. While hydrogen selective membranes have been considered for applications in these areas, their use has generally been limited due to cost and hydrogen embrittlement of the metal. The most popular metal used for hydrogen separation has been palladium or its alloys. Indeed, the palladium/hydrogen system has been studied extensively, beginning with the early work of Graham well over a hundred years ago<sup>1</sup>. While palladium is an attractive membrane material due to its ability to readily dissociate molecular hydrogen to atomic hydrogen at its surface, several problems remain.

increasing

First, palladium has an  $\alpha$ - $\beta$  phase transition (a crystal structure change in the metal) that is dependent upon hydrogen concentration in the metal at temperatures below  $300^\circ\text{C}^2$ . Expansion and contraction of the lattice from the phase transformation with varying hydrogen concentrations leads to embrittlement and fracture of the metal. Some control of this problem can be obtained by alloying with silver. Inclusion of silver into the palladium significantly reduces the critical temperature and pressure of the  $\alpha$ - $\beta$  phase transition<sup>3</sup>. While this does increase the longevity of the membranes, these materials are expensive. Furthermore, the bulk transport of hydrogen in face-centered cubic (fcc) metals such as palladium and its alloys remains considerably lower than in a number of refractory, body-centered cubic (bcc), metals<sup>4,5</sup>. As observed in Figure 1, zirconium, niobium, tantalum, and vanadium all have significantly higher bulk hydrogen permeabilities than does palladium<sup>6</sup>. Unfortunately, the direct replacement of palladium for cheaper refractory metals as membranes is hindered because these metals form oxide layers and the reduced surface reaction limits the hydrogen flux<sup>6</sup>.

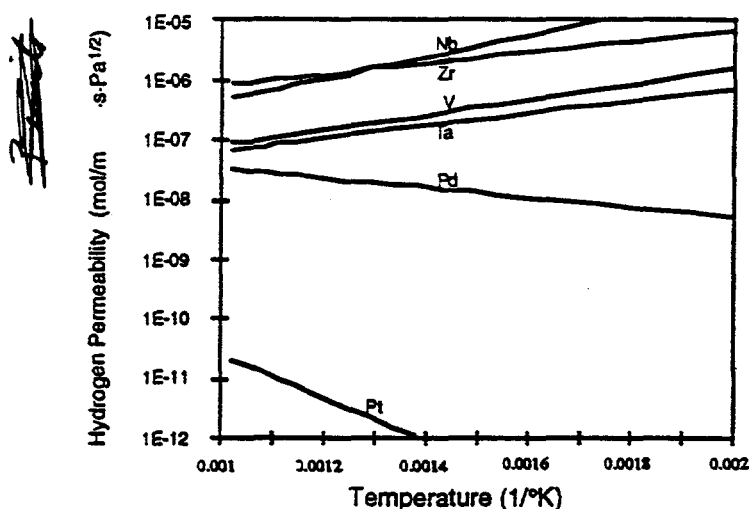


Figure 1. The bcc-refractory metals have a higher transport rate than palladium or platinum.

To exploit the rapid bulk diffusion of hydrogen in the refractory metals, a composite structure can be constructed where palladium is placed on each side of the bcc-metal. This allows the dissociation of the molecular hydrogen by the surface palladium layer, transport through the refractory metal bulk, and finally reassociation on the opposite surface. This composite membrane is shown in Figure 2. Such a structure has several advantages. First, greater overall hydrogen fluxes are expected because bulk diffusion is not limited by the fcc structure of palladium. The membrane structure can then be thicker, yielding improved mechanical stability while still providing acceptable gas fluxes. Second, because refractory metals are significantly cheaper than palladium and only a surface layer of palladium is required, these structures are much more economical. Finally, while the Group VB metals are also subject to embrittlement, the regime where this is a problem is well below room temperature<sup>7,8</sup>. Should the surface palladium layer develop defects, this would not render the membrane useless since it would merely expose a small area of the refractory metal. The obvious advantages of a composite metal membrane have not escaped past investigators. Indeed, about 30 years ago, Makrides filed a patent for plating foils of Group VB metals with thin layers of palladium<sup>9</sup>. In recent years, additional patents have been filed by other groups for similar structures<sup>10,11,12</sup>. While it is clear that viable

composite metal membranes have been constructed, improvements of the process are still required to make these structures more efficient. Removal of the refractory metal surface oxide layer is a critical requirement. Various chemical and mechanical techniques have been used to achieve this but most allow regrowth before coating with the top palladium or palladium alloy. Another concern is the quality of the palladium or alloy layer.

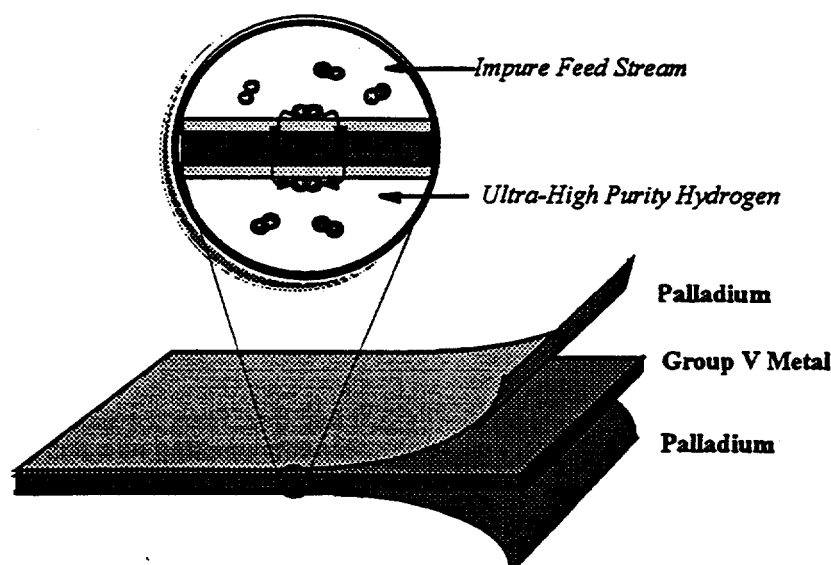


Figure 2. The composite membrane has thin layers of palladium on both sides of a Group V metal foil.

To address the need for enhanced hydrogen separation techniques using metal membranes, we have recently begun investigating composite structures. The objectives for development of a membrane foil were (1) obtaining a highly clean surface on the refractory metal foil, (2) forming a palladium coating without subsequent contamination, and (3) giving attention to the purity and crystallinity of the coated layer. To achieve this, foils of tantalum were cleaned by ion milling in a vacuum chamber and then immediately coated with palladium in the same chamber. These foils yielded exceptionally high hydrogen flow rates.

#### Procedure:

##### Membrane Setup:

The foils provided by the instructor should be cut into 1/2 in diameter discs that will fit into the VCR® components. Note that fingerprints will reduce the performance of the foils; a quick wash in a common solvent, such as methanol, will remove any fingerprints and residual oils. Place a disc in-between a male and a female VCR® and tighten to make a good seal, as shown in Figure 3. Metal tubing from the VCR® fittings should extend at least 6 inches on each side because the VCR® will be heated to at least 300° C. Past the 6 inches metal or plastic tubing can be used. This tubing must be long enough to reach the hydrogen tank on one side and to the flow rate measurement system on the other. Do not expose the foil to hydrogen until after the heat-up.

91 explaining nature of experiment

define

beyond

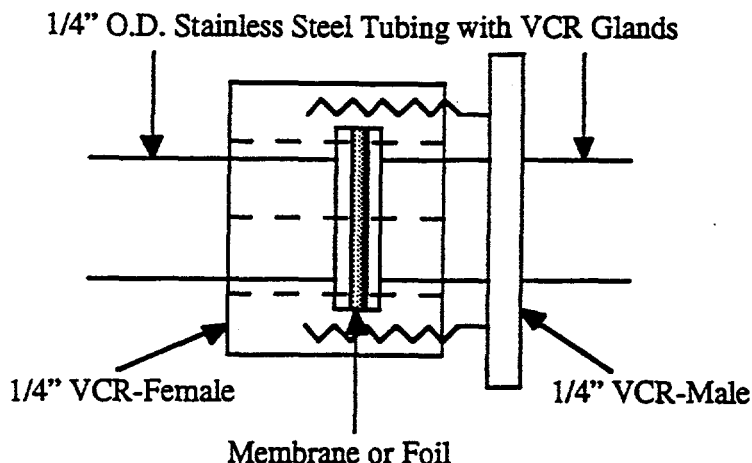


Figure 3. The membrane or foil is used in place of the VCR® washer.

#### Membrane Heat-up:

A thermocouple is first placed on the VCR® and then both the thermocouple and VCR® are wrapped with heat tape. The thermocouple is connected to a readout. The heat tape is connected to a variable power supply. The overall system schematic is illustrated in Figure 4. The power supply should be adjusted for a heat rate of 10°C/Min. The power supply will need to be adjusted to stabilize the system between 300 and 350°C. The heat tape will smell as it is heated, especially when the tape is used for the first time, so doing this in a hood is preferred.

*Flow removing air from supply side.*

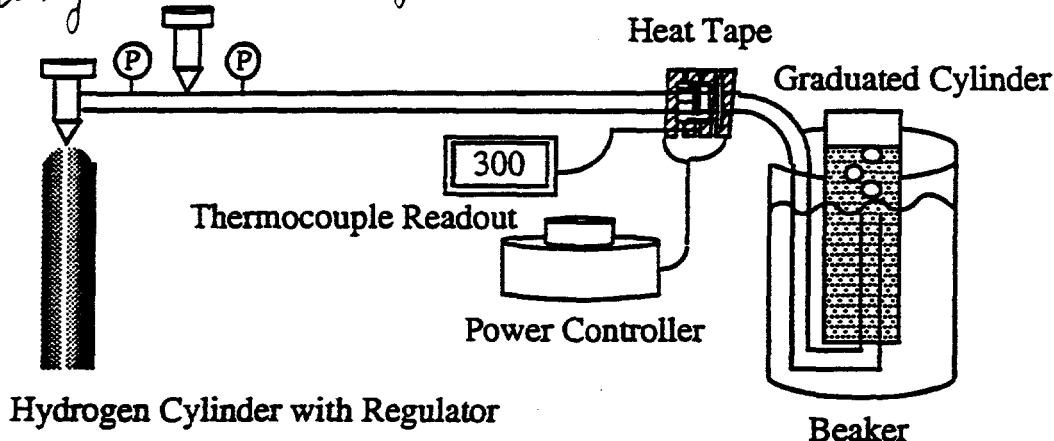


Figure 4. The hydrogen transported through the membrane will displace the water in the graduated cylinder.

#### Flow Rate Measurements:

A flow rate can be measured by taking the outlet hose of the VCR® system and placing it under water into a graduated flask that has been inverted and filled with water. Bubbles from the hose will replace the water at a given rate, calculated as the volume displaced in a given length of time. This rate should be determined and compared for the three foils.

### Notes to the Instructors:

One foil can be measured at a time if VCR<sup>®</sup> units are limited. For a more direct and dramatic comparison the 3 foils can be measured in 3 VCR<sup>®</sup> systems at the same time by wrapping all three units in a single heat tape and measuring the temperature at the center of the three units. Three graduated cylinders and beakers should be used to allow for a direct comparison of the flow rates from each of the foils.

Many of the materials used in this experiment are readily available in most standard chemistry laboratories or stockrooms. The Vanadium and Palladium foil can be purchased through a specialty metal supplier, such as Goodfellow Corporation (800 Lancaster Avenue, Berwyn, PA 19312-1780, Ph. 800-821-2870). The composite membrane is available from Generex, Inc. (P.O. Box 84, Tryon, NC 28782, Ph. 704-863-4245). The VCR<sup>®</sup> fittings are available from many valve and fitting sellers; the CAJON Company can direct to the local reseller (9760 Shepard Road, Macedonia, OH 44056)

Finally, hydrogen is an extremely efficient fuel that can easily burn in air and can represent an explosion hazard, as all fuels can. It should be handled with particular care and concern and only by those trained in hydrogen safety.

### References:

- systems and safety?*
- 
- <sup>1</sup>T. Graham, *Phil. Trans. Roy. Soc. (London)* **156** (1866) 415.
- <sup>2</sup>Wicke, E.; Brodowsky, H.; Züchner in *Hydrogen in Metals II*, Topics in Applied Physics, Vol. 29, G. Alefeld and J Völkl, Eds., Springer-Verlag: New York, 1978, p. 73.
- <sup>3</sup>Shu, J., Grandjean, B. P. A.; Van Neste, A.; Kaliaguine, S. *Can. J. Chem. Eng.* **69** (1991) 1036.
- <sup>4</sup>Alefeld, G.; Völkl, J. *Hydrogen in Metals I*, G. Alefeld and J. Völkl, eds., Springer-Verlag: New York, 1978, 321.
- <sup>5</sup>Buxbaum, R. E.; Marker, T. L. *J. Membrane Sci.* **85** (1993) 29.
- <sup>6</sup>Steward, S. A. *Review of Hydrogen Isotope Permeability through Materials* (1983) Lawrence Livermore National Laboratory Report # UCRL-53441.
- <sup>7</sup>Owen, C. V.; Scott, T. E. *Metallurgical Trans.* **3** (1972) 1715.
- <sup>8</sup>Schober, T.; Wenzl, H. in *Hydrogen in Metals II*, Topics in Applied Physics, Vol. 29, G. Alefeld and J Völkl, Eds., Springer-Verlag: New York, 1978, p. 11.
- <sup>9</sup>Makrides, A. C.; Wright, M. A.; Jewett, D. N.; Separation of hydrogen by permeation, US Patent 3,350,845, Nov. 7, 1967.
- <sup>10</sup>Buxbaum, R. E., Composite metal membrane for hydrogen extraction, US Patent 5,215,729, June 1, 1993.
- <sup>11</sup>Edlund, D. J., Hydrogen-permeable composite-metal membranes, US Patent 5,139,541, Aug. 18, 1992.

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<sup>12</sup>Edlund, D. J., Composite hydrogen separation metal membrane, US Patent 5,393,325, Feb. 28, 1995.

### **Biographies:**

#### **Dr. Robert C. Dye**

Dr. Dye is currently the project leader for the high temperature membrane effort at Los Alamos National Laboratory. He also leads the Lab's thin-film phosphor efforts. His work at Los Alamos has focused on thin-film depositions including zeolites, high dielectrics, superconductors, and phosphors. He has contributed significantly in these areas with over one hundred publications and presentations. Dr. Dye and his teams have filed six patents dealing with the deposition and diagnostics of thin-film coatings, some of which have been fully commercialized. In 1995, he received the Industrial Partnership Award for outstanding technology transfer. He received a B.S. in Chemistry at the University of Central Missouri State in 1983 and a Ph.D. in Physical Chemistry from the University of Nebraska in 1989. He joined the Los Alamos National Laboratory in 1989 and is now part of the Materials Science and Technology Division.

#### **Dr. Thomas S. Moss, III**

Dr. Moss is currently a Director's Funded Post-doctoral Fellow with the Materials Science and Technology Division at Los Alamos National Laboratory. His work at Los Alamos has involved high temperature metal membranes and metal organic chemical vapor deposition of thin film phosphors. Dr. Moss received his Bachelor's of Materials Engineering in 1992 and Doctor of Philosophy in Ceramic Engineering in 1995 from the Georgia Institute of Technology. He joined the Coatings and Polymers Group at Los Alamos in 1995. Over the past six years, he has authored over 30 papers regarding high temperature membranes and the chemical vapor deposition of phosphors and ceramic materials.



A knowledge of Hydrogen safety is required for this experiment.

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- Hydrogen is an extremely flammable fuel that releases large amounts of heat when burned.
- In large amounts, Hydrogen can cause asphyxiation.
- Always work within the safety guidelines of your institution.

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There are several objectives for this experiment:

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- To learn about hydrogen's interaction with metals,
- To study catalytic and transport properties of hydrogen, and
- To engineer composite materials for the transport of hydrogen.

Hydrogen promises an unlimited, clean, efficient energy source.

---

- World oil consumption continues to grow, particularly in the developing East;
- World crude oil reserves are expected to peak after the year 2000 (i.e., 2005-2010);
- Now is the time to begin considering alternative energy sources, applications, and infrastructure.

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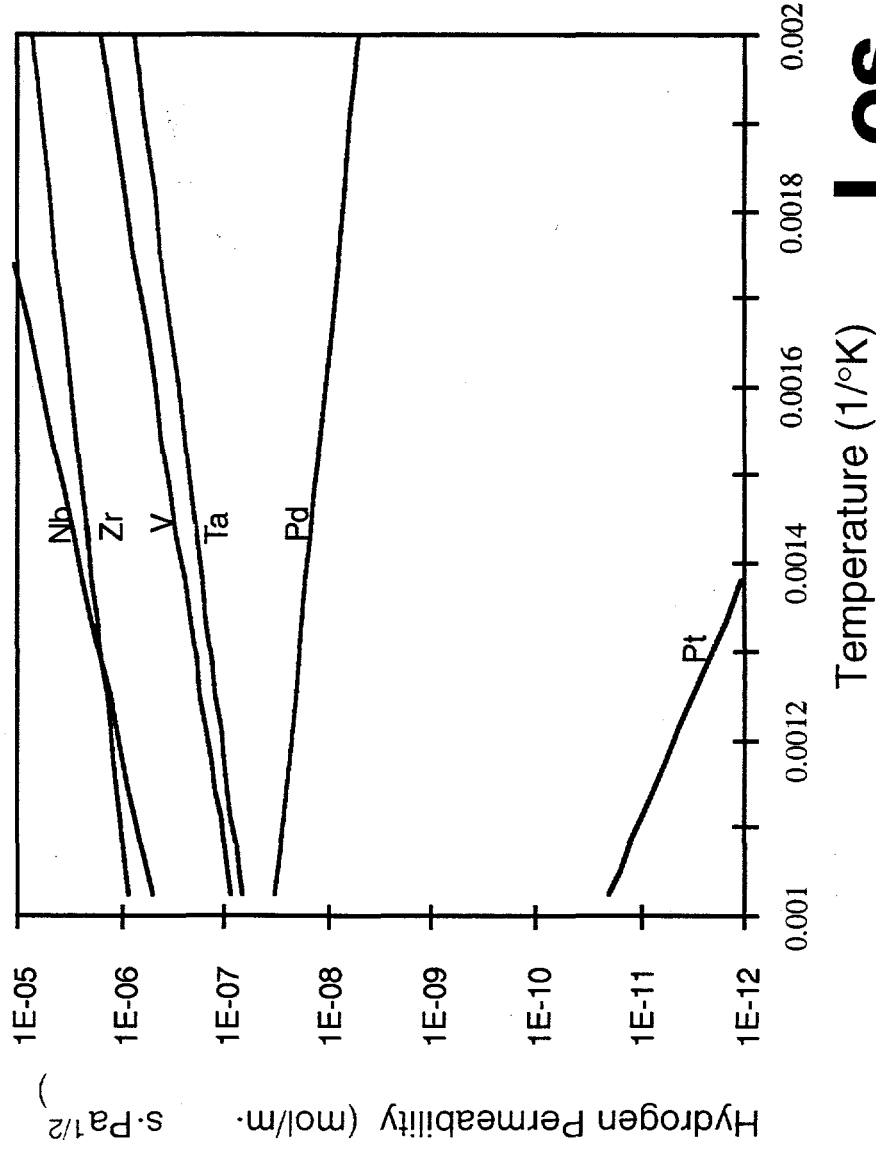
There are several inherent problems with Palladium and Palladium Alloys for hydrogen separation.

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- $\alpha$ - $\beta$  Palladium phase transformation at 300°C causes embrittlement and fracture.
- Alloying with Silver can reduce the temperature of this transformation and reduce embrittlement but is expensive.
- Bulk transport of hydrogen through fcc metals (i.e., Pd) is slow compared to bcc-refractory metals (i.e., Zr, Nb, Ta, V).

The hydrogen permeability of bcc-refractory metals is significantly higher than that of fcc metals.

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The composite membrane uses the advantageous properties of both Palladium and Vanadium.

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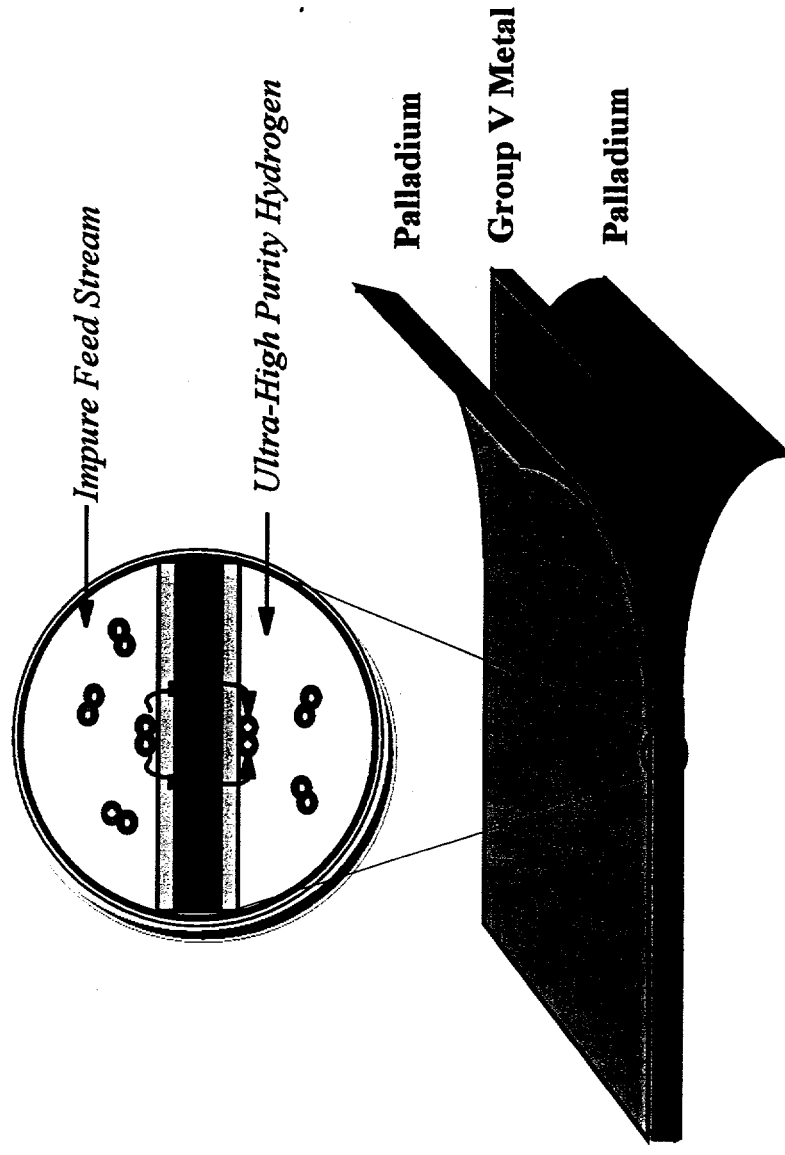
- First Palladium Layer: Catalyzes the breakup of Hydrogen molecules into Hydrogen atoms.
- Vanadium Foil: Transports Hydrogen atoms faster than Palladium.
- Second Palladium Layer: Re-assembles Hydrogen atoms into Hydrogen Molecules

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Hydrogen selectively passes through the multilayer metal membrane.

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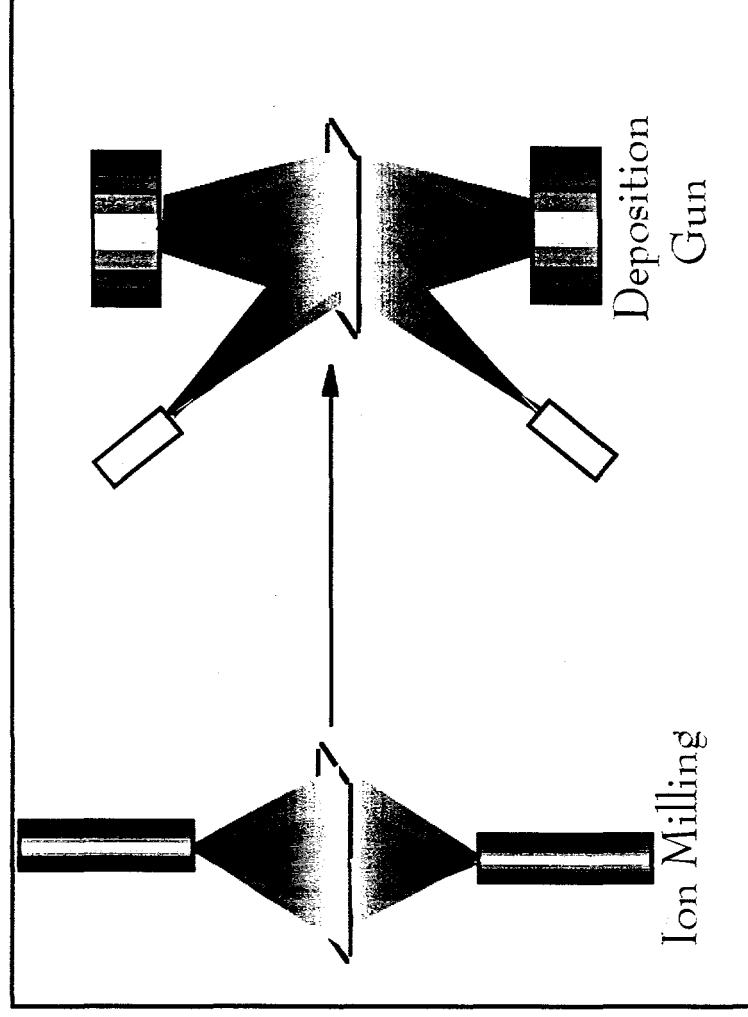


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The foil is cleaned by ion milling before  
the Palladium is sputter deposited.

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Vacuum Chamber

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To conduct this experiment, several pieces of equipment are needed.

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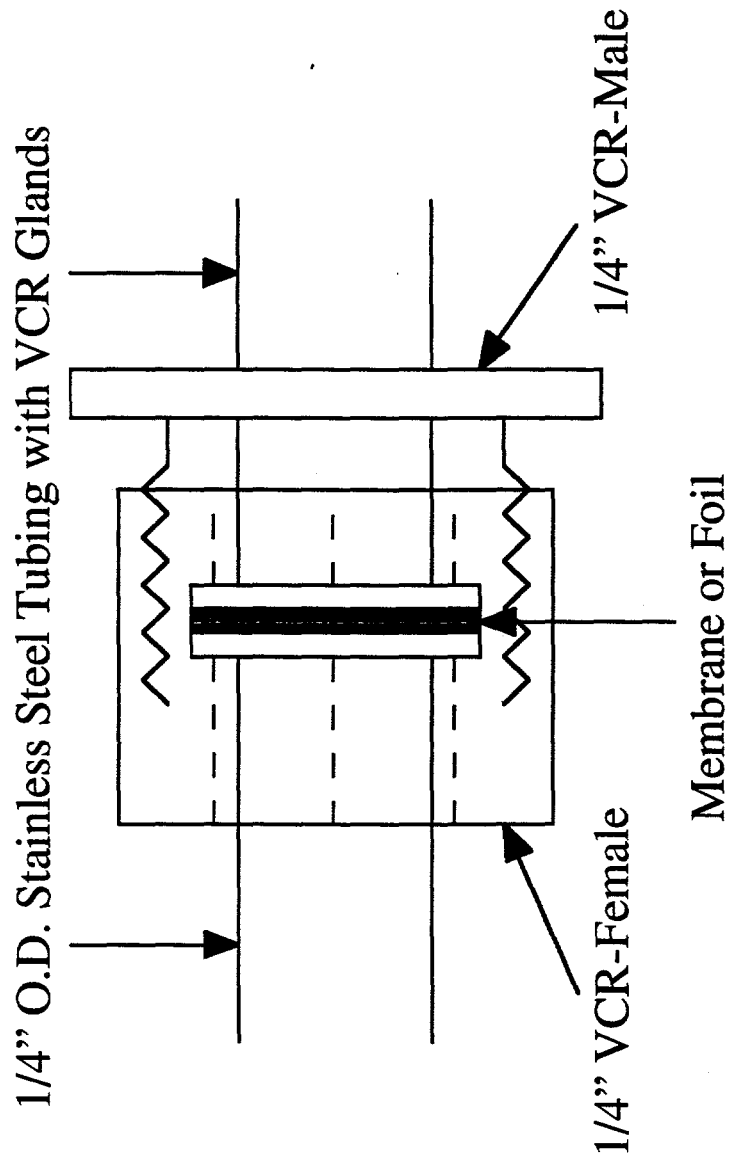
- Heating tape
- Thermocouple
- Temperature Readout
- Power Controller
- Beaker
- Graduated Cylinder
- Food Coloring (Optional)
- VCR Fittings
  - Male and Female
- Tubing
- Hydrogen Cylinder with Regulator
- Palladium Foil
- Vanadium Foil
- Composite Foil

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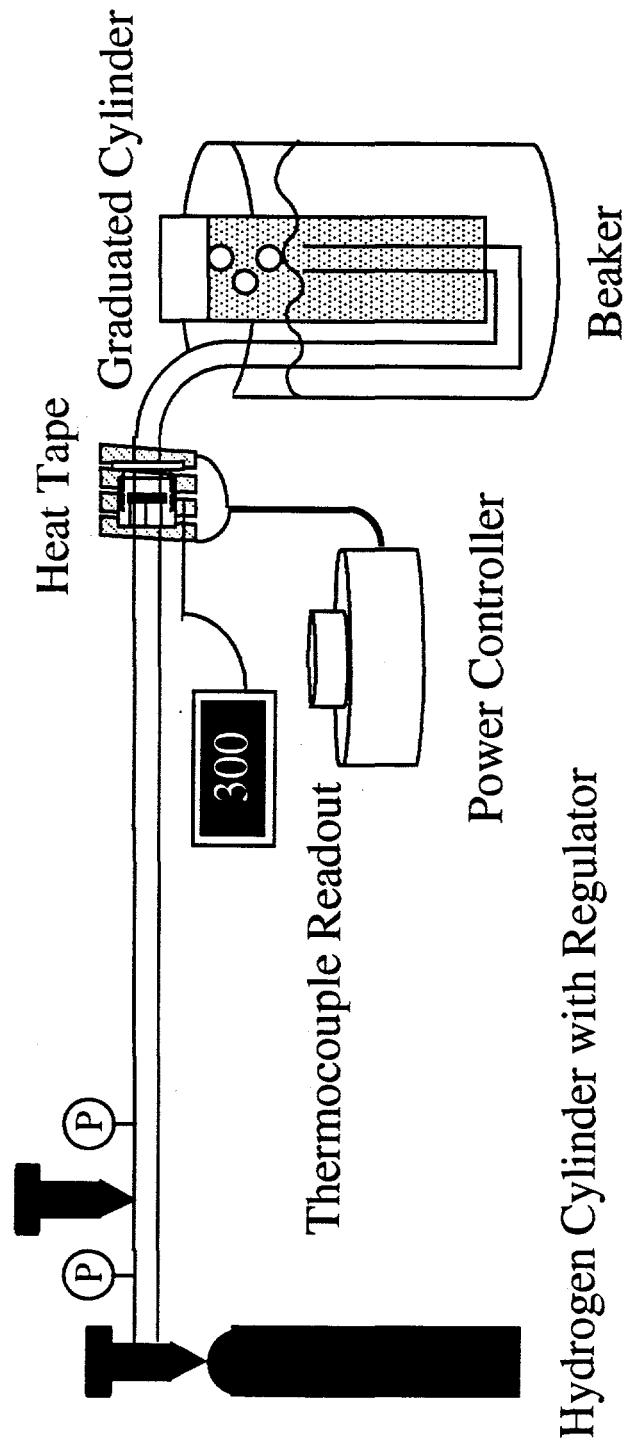
The membrane seal is made by a VCR fitting.

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The experimental set-up allows Hydrogen gas from the membrane to displace water in a graduated cylinder.

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# Procedure

---

- Prepare inverted graduated cylinder in Water filled beaker;
- Load and seal membrane in VCR holder;
- Attach VCR holder to H<sub>2</sub> tank and to graduated cylinder;
- Heat the membrane to 300°C;
- Apply H<sub>2</sub> pressure from regulator;

## Procedure continued

---

- After flow has stabilized, observe gas level in graduated cylinder and start clock;
- Take readings of gas volume and time until the gas occupies most of the cylinder;
- Remove  $H_2$  pressure and cool membrane;
- Repeat using pure Palladium and Vanadium membranes.

# Calculations

---

- Flow rate or Hydrogen transport rate is given by:

$$Q_{H_2} = \frac{Volume_{Final} - Volume_{Initial}}{time_{Final} - time_{Initial}}$$

Q: cm<sup>3</sup>/min    Volume: cm<sup>3</sup>    time: minutes

- Compare transport rates for pure Palladium, pure Vanadium, and composite membrane.

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In this experiment, the Hydrogen flow rate through the membrane is governed by Sievert's Law.

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$$Q_{H_2} = \left( \frac{J}{\ell} \right) \cdot \left( \sqrt{P_f} - \sqrt{P_p} \right) \cdot A$$

$Q_{H_2}$ : Flow rate	(cm <sup>3</sup> /min)
J: Permeability	(cm <sup>2</sup> /(min torr <sup>0.5</sup> ))
ℓ: Membrane Thickness	(cm)
$P_f$ : Feed Pressure	(torr)
$P_p$ : Permeate Pressure	(torr)
A: Membrane Area	(cm <sup>2</sup> )

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# Conclusions

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- Purification by metal membranes involves catalytic splitting of  $H_2$  molecules, transport of H atoms and rejoining H atoms to  $H_2$ .
- It is possible to engineer a composite membrane that utilizes the good catalytic and transport properties inherent to metals.
- This composite membrane has higher flow rates than either of the constituents.

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## **ELECTROLYTIC PRODUCTION OF HYDROGEN UTILIZING**

**PHOTOVOLTAIC CELLS** Mark Daugherty and Christine Zawodzinski, Los Alamos National Laboratory

This demonstration illustrates the use of photovoltaics to produce hydrogen by the electrolysis of water. The system has four components: a photovoltaic panel, an electrolyzer, a dryer to remove water from the product hydrogen gas and a hydride canister to store the hydrogen. Hydrogen production is proportional to the current output from the photovoltaic panel, provided the required voltage can be maintained. The electrolyzer uses a proton exchange membrane to produce hydrogen and oxygen from water. The oxygen is vented and the hydrogen is dried and then stored in a metal hydride canister. Systems of this type are able to sustainably produce hydrogen fuel as long as water and sunlight are available.

# Electrolytic Production of Hydrogen Utilizing Photovoltaic Cells\*

Mark A. Daugherty and Christine Zawodzinski

Los Alamos National Laboratory

Los Alamos, New Mexico

**Key Words:** Electrolyzer, Renewable Hydrogen Production

**Prerequisite Knowledge:** Knowledge of basic electrochemistry is helpful but not required. Knowledge of basic hydrogen safety is required, references are provided to assist in developing this knowledge.

**Objective:** To observe the performance of a small renewable hydrogen production system. To measure the efficiency of a single cell proton exchange membrane electrolyzer and to develop a basic understanding of its operation.

## Equipment

1. (2) multimeters or a data acquisition system
2. solar array (3.0 V and 1.9 A maximum outputs)
3. copper wire
4. (2) copper connectors
5. (1) electrolyzer cell containing:
  - (2) plexiglass end plates
  - (2) 316 stainless steel current collectors  
(one gold plated - nickel strike followed by 0.0005" gold)
  - (1) catalyzed polymer electrolyte membrane
  - (4) 0.030" thick carbon papers
  - (2) fiber reinforced silicone gaskets
  - (2) Teflon gaskets
  - (4) insulating washers
  - (4) insulating pins
  - (8) sets of stainless steel bolts, nuts and washers
6. distilled water
7. tubing and tubing connectors, suitable for hydrogen operation
8. pressure vessel suitable for hydrogen  
(150 psi maximum working pressure)
9. (1) hydrogen pressure relief valve (set at 100 psi)
10. (1) control rheostat
11. (1) hydrogen pressure gauge

\* This work was supported by the U.S. Department of Energy, Office of Utility Technologies, Hydrogen Program Office

## **Introduction:**

Hydrogen has the potential to serve as both an energy storage means and an energy carrier in renewable energy systems. When renewable energy sources such as solar or wind power are used to produce electrical power, the output can vary depending on weather conditions. By using renewable sources to produce hydrogen, a fuel which can be stored and transported, a reliable and continuously available energy supply with a predictable long-term average output is created.

Electrolysis is one method of converting renewable energy into hydrogen fuel. In this experiment we examine the use of an electrolyzer based on polymer-electrolyte membrane technology to separate water into hydrogen and oxygen. The oxygen is vented to the atmosphere and the hydrogen is stored in a small pressure vessel.

## **Basic Safety Considerations:**

It is necessary to consider safety in every step of the design, fabrication, assembly and operation of a hydrogen system. For the present system major safety issues include: 1) ensuring that the maximum operating current of the electrolyzer is never exceeded. 2) ensuring that there are no gas leaks in the system. 3) ensuring that the maximum operating pressure of the system is never exceeded. 4) excluding possible ignition sources from the area of the oxygen and hydrogen vents, and 5) separation of the hydrogen and oxygen vents. Reference 1 provides a general description of hydrogen and hydrogen containers and references 2-4 are intended to provide an introduction to hydrogen safety. It is the responsibility of the experimenter to develop a working knowledge of the appropriate hydrogen safety requirements.

## **Experimental Apparatus:**

A schematic of the experimental apparatus is shown in Figure 1. Power for the electrolyzer is provided by the photovoltaic array. A control rheostat is located between the array and the electrolyzer to control the input power to the electrolyzer. Oxygen from the electrolyzer is vented to the atmosphere and the hydrogen is stored in a pressure vessel. A pressure relief valve is located on the hydrogen storage vessel. A pumpout valve is located in the hydrogen tubing between the electrolyzer and the storage vessel.

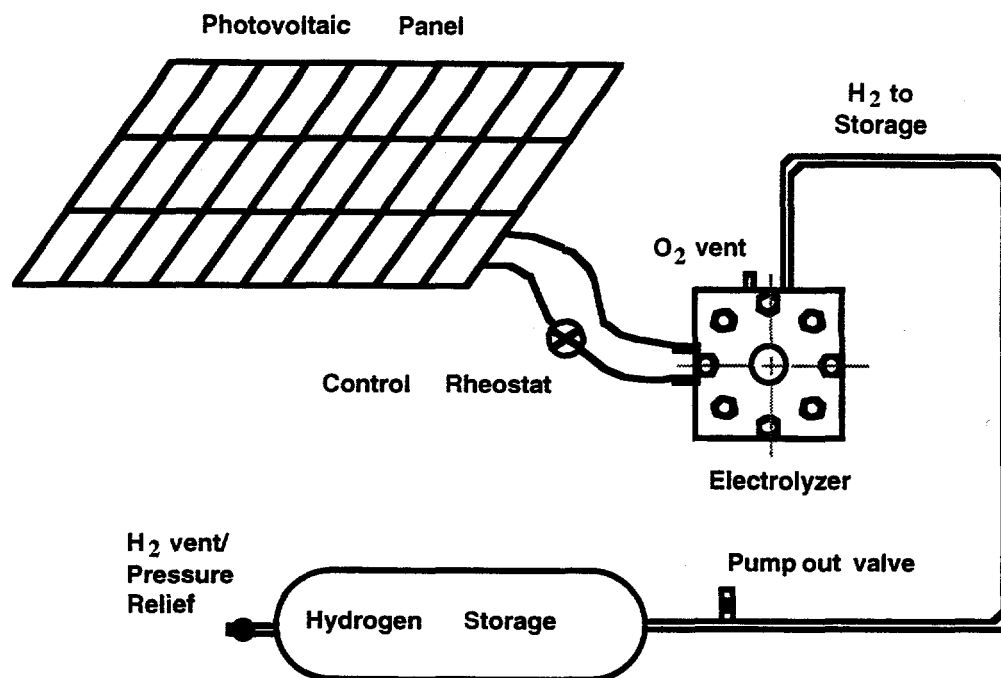


Figure 1: Electrolyzer system schematic

### Solar Array:

The electrolyzer used in this experiment is designed to operate at a current density of  $250 \text{ mA/cm}^2$  across the membrane. If currents significantly larger than the design current are applied across the membrane, the voltage drop will increase rapidly as shown by the solid curve in Figure 2. As the voltage rises excess heating will occur and it is possible to damage the membrane. This must be avoided as it may allow the hydrogen and oxygen to mix, creating a potential safety hazard.

The output from a photovoltaic array is shown schematically by the dashed line in Figure 2. By sizing the photovoltaic array so that the maximum short circuit current of the array ( $I_{sc}$ ) is below the maximum operating current of the electrolyzer ( $I_{max}$ ) one can ensure that the electrolyzer will never operate above its maximum rated current.  $I_{max}$  will vary for different catalyzed membrane assemblies and also depends on the temperature of the cell. For the assembly used in this experiment the maximum operating current density is  $300 \text{ mA/cm}^2$ . The photovoltaic array and the electrolyzer will operate at the point where the two curves cross. This is indicated by  $V_{op}$  and  $I_{op}$  in the figure.

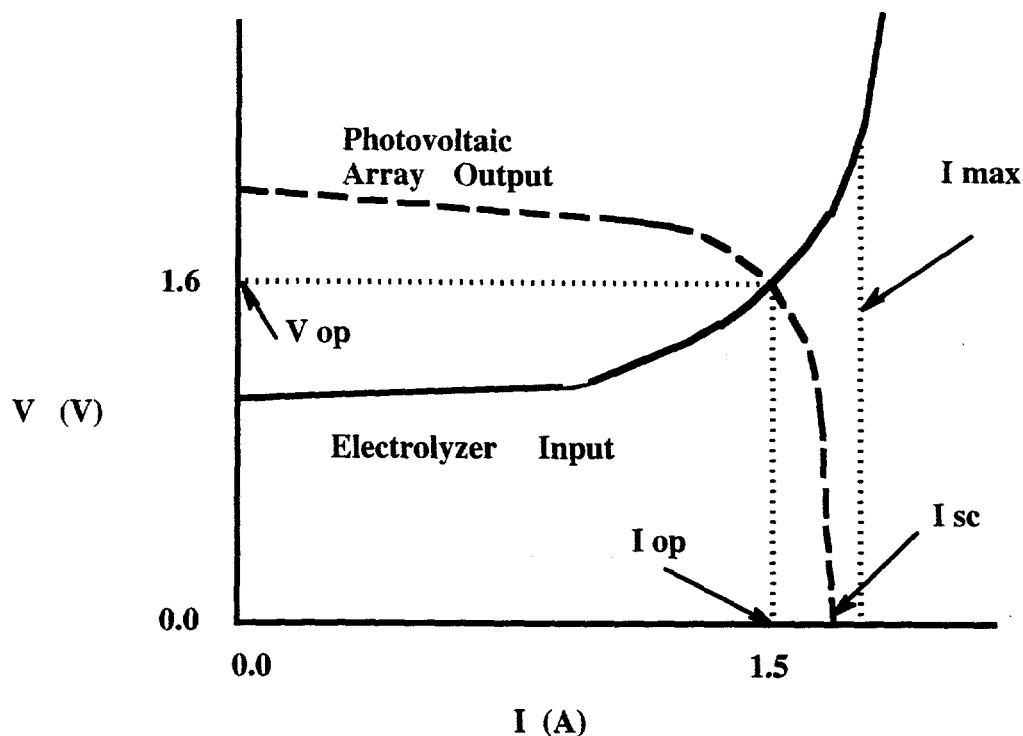


Figure 2: Photovoltaic array sizing

The photovoltaic array was assembled by soldering individual solar cells together. Seven cells were soldered together in series to produce the required voltage and eight of these seven cell stacks were then soldered together in parallel to provide the required current. Three mil copper foil was used to connect the cells in series by attaching the front connector pads of one cell the back connector pads of the next cell. Copper wire (22 gage stranded) was used to connect the stacks in parallel. One end of a standard banana plug wire was cut off and soldered to the array wiring and the other end was used to connect the array to the electrolyzer. The array and control rheostat were mounted on a standard white board purchased at the local hardware store. The arrangement is shown schematically in figure 3. Solar cells are available for educational purposes and can be obtained while supplies last. Marcia Zalbowitz at Los Alamos National Laboratory is the contact person for hydrogen educational activities.

### Electrolyzer:

The polymer-electrolyte membrane is at the heart of this electrolyzer. In this case, the membrane is a specially treated polymer that conducts protons or other cations, but not anions. A specific catalyst is applied to each side of the membrane to facilitate the water electrolysis reactions, which are shown in Figure 4. On the anode side where oxygen is produced, the catalyst used is

ruthenium oxide and on the cathode side where hydrogen is evolved, the catalyst is platinum supported on carbon black.

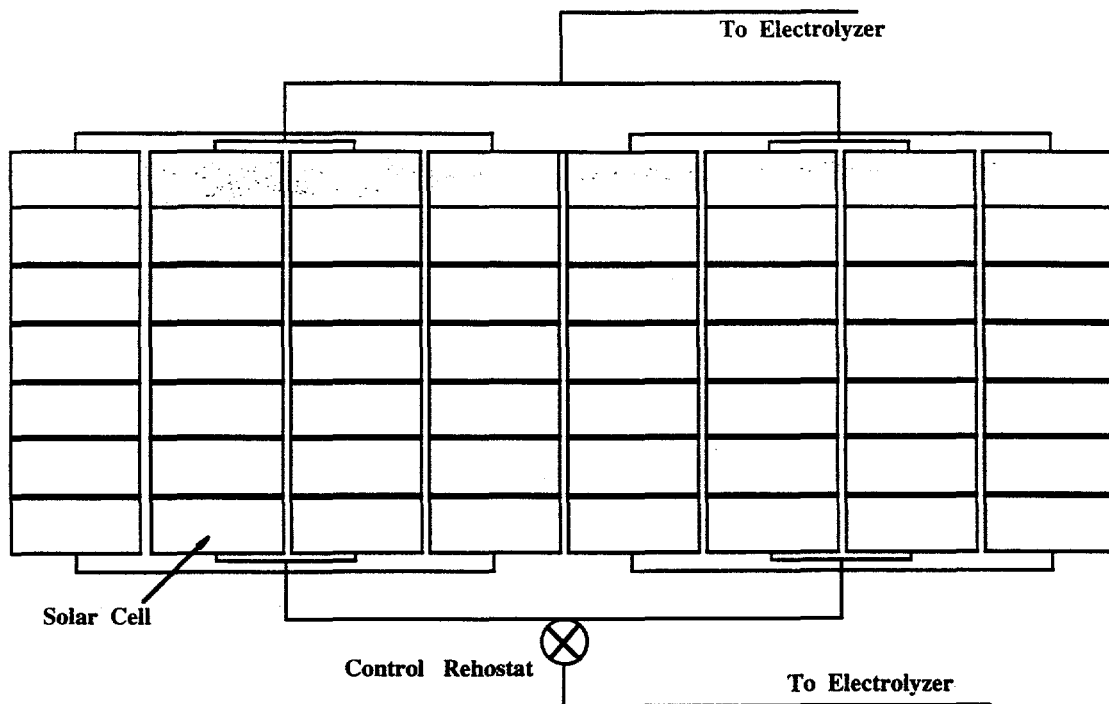


Figure 3: Schematic of Photovoltaic Array

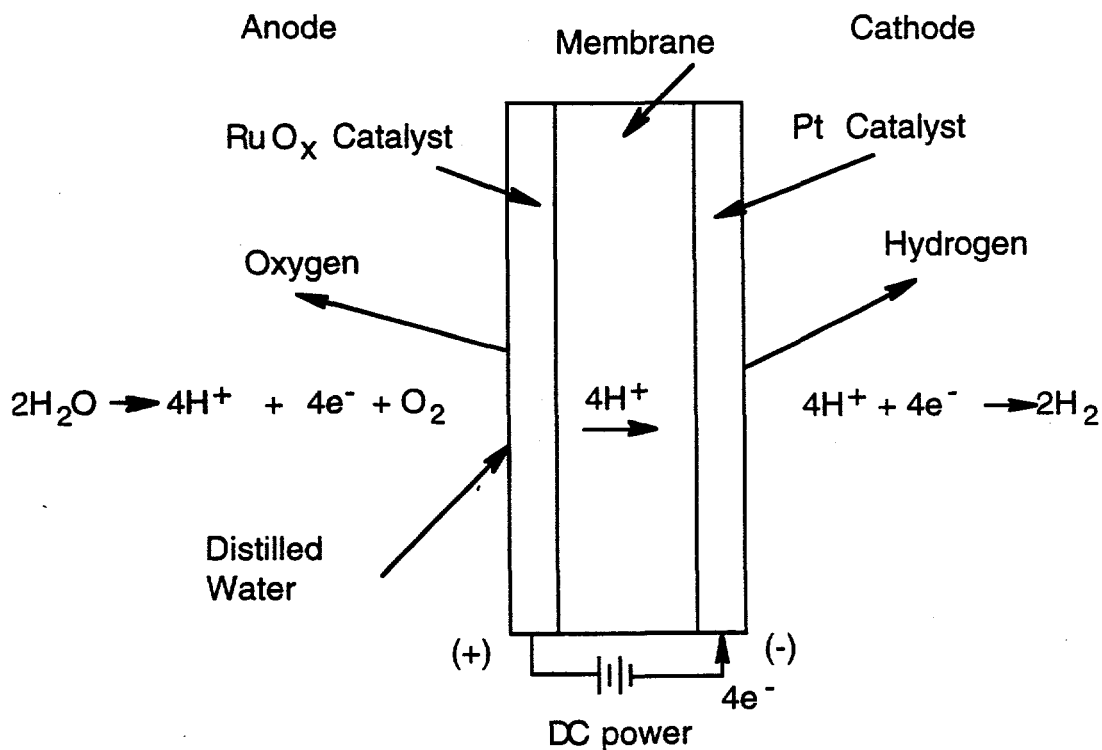
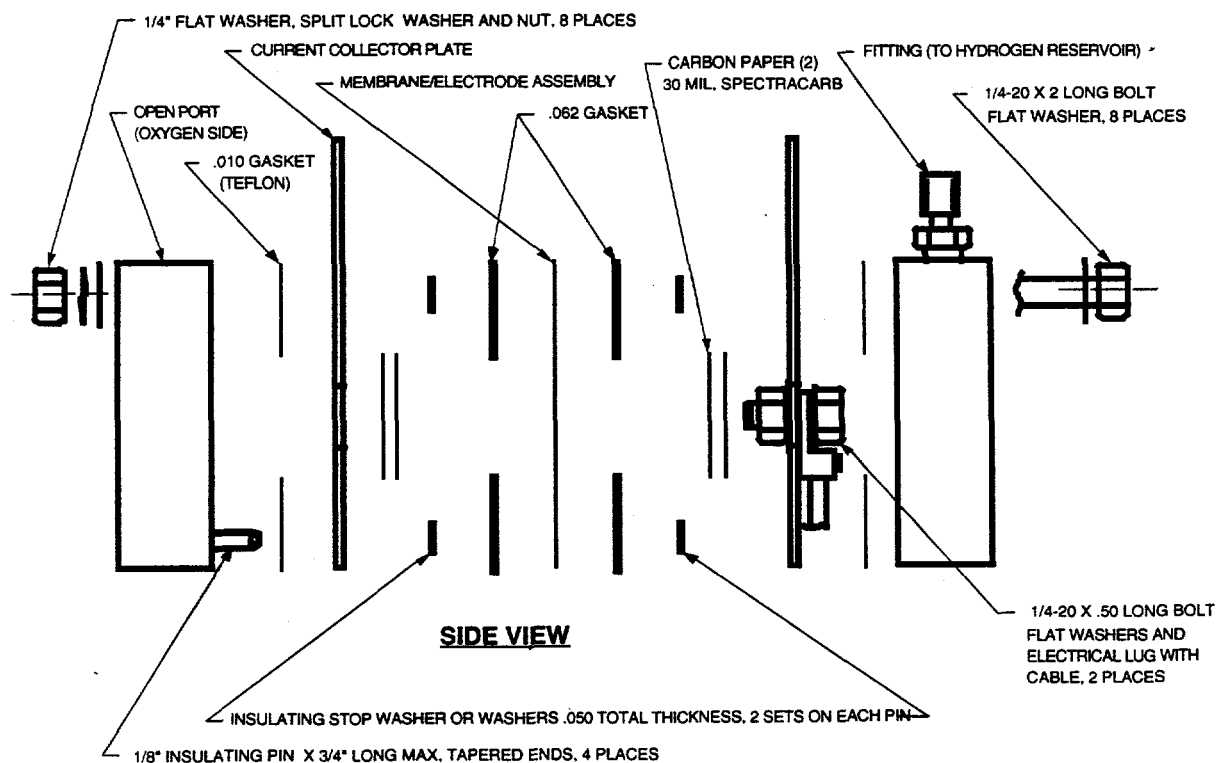


Figure 4: Water electrolysis reactions

A schematic of the electrolyzer is shown in Figure 5. Electrical connections to the electrolyzer are made to the two 316 stainless steel current collector plates. On the anode side (positive lead) the collector is gold plated to reduce corrosion in the oxygen environment. Carbon paper is used to provide electrical contact between the current collectors and the catalyst layers on the membrane. While the carbon paper will corrode relatively quickly on the anode side it is less expensive than a more durable titanium screen. The carbon paper on the anode side will have to be replaced as it wears away. In addition to electrical contact the carbon paper provides a pliable mechanical support between the current collectors and the catalyzed membrane assembly. Fiber-reinforced silicone gaskets and Teflon gaskets are used for sealing and insulating washers are used to fix the compression of the inner silicone gaskets. The entire assembly is clamped together using stainless steel bolts.

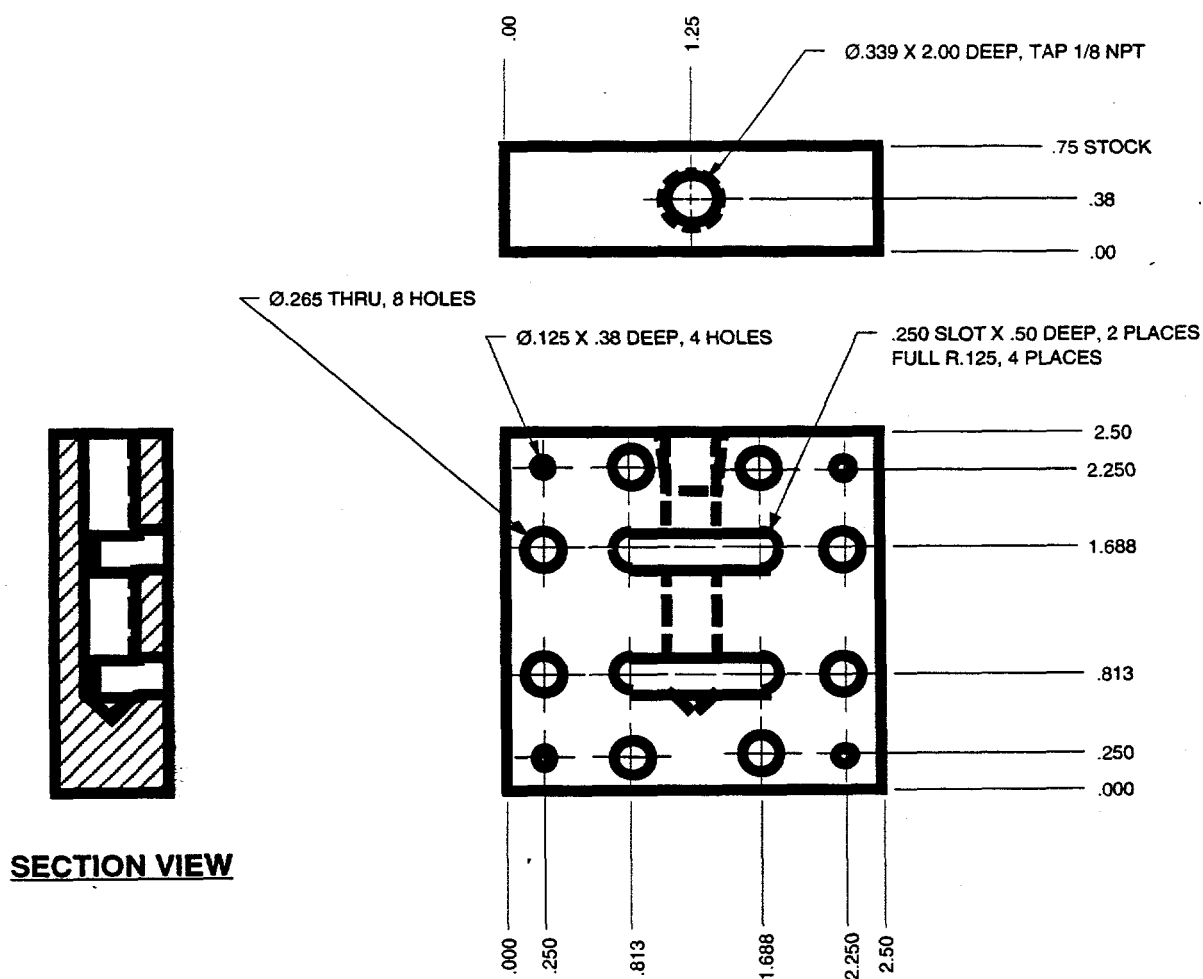
Rubber gloves should be worn during assembly to protect the materials. Assembly begins by pressing the four insulating pins into the anode end plate. The drawing for the end plate is shown in figure 6.



NOTE: ASSEMBLY IS SYMMETRICAL AND NOT ALL CALLOUTS ARE DUPLICATED.

Figure 5: Electrolyzer Assembly (Exploded View)

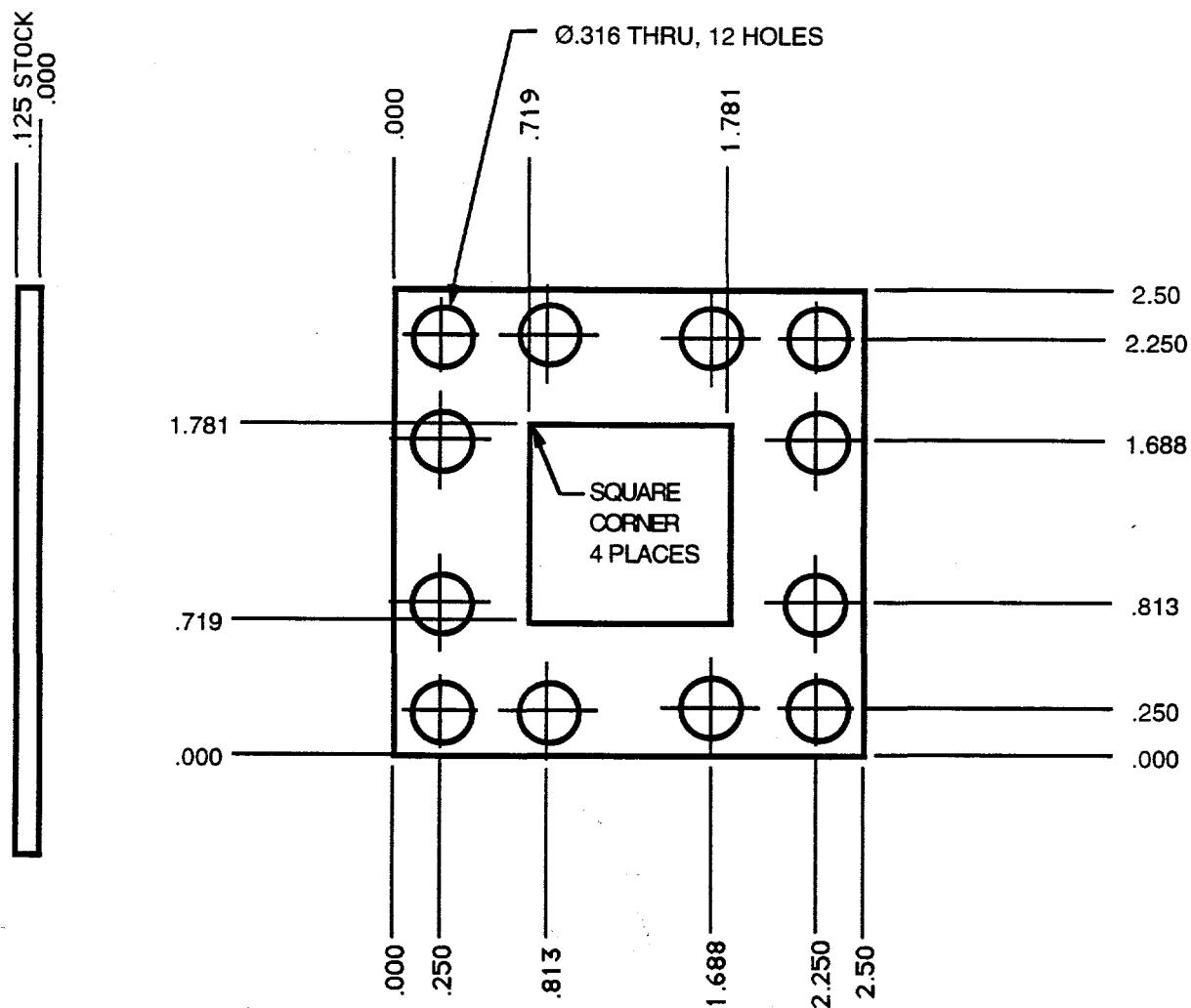
Then the Teflon gasket is slipped over the pins followed by the gold plated current collector plate. The gasket template is shown in figure 7 and the current collector drawing in figure 8. Next a fiber-reinforced silicone gasket is placed on the stack and two sheets of carbon paper are fitted into the middle of the gasket. The template for the carbon paper is shown in figure 9. The four insulating washers are placed in the corner holes of the gasket over the pins to fix the gasket compression. The membrane is then placed on the stack with the ruthenium oxide side toward the gold plated current collector. The procedure is continued for the other side of the electrolyzer, whose construction is symmetrical with that of the first side.



SCALE: 1/1, MAT'L: PLEXIGLAS (PMMA) .75" THICK, QTY: 2 EACH

Figure 6: Electrolyzer End Plate

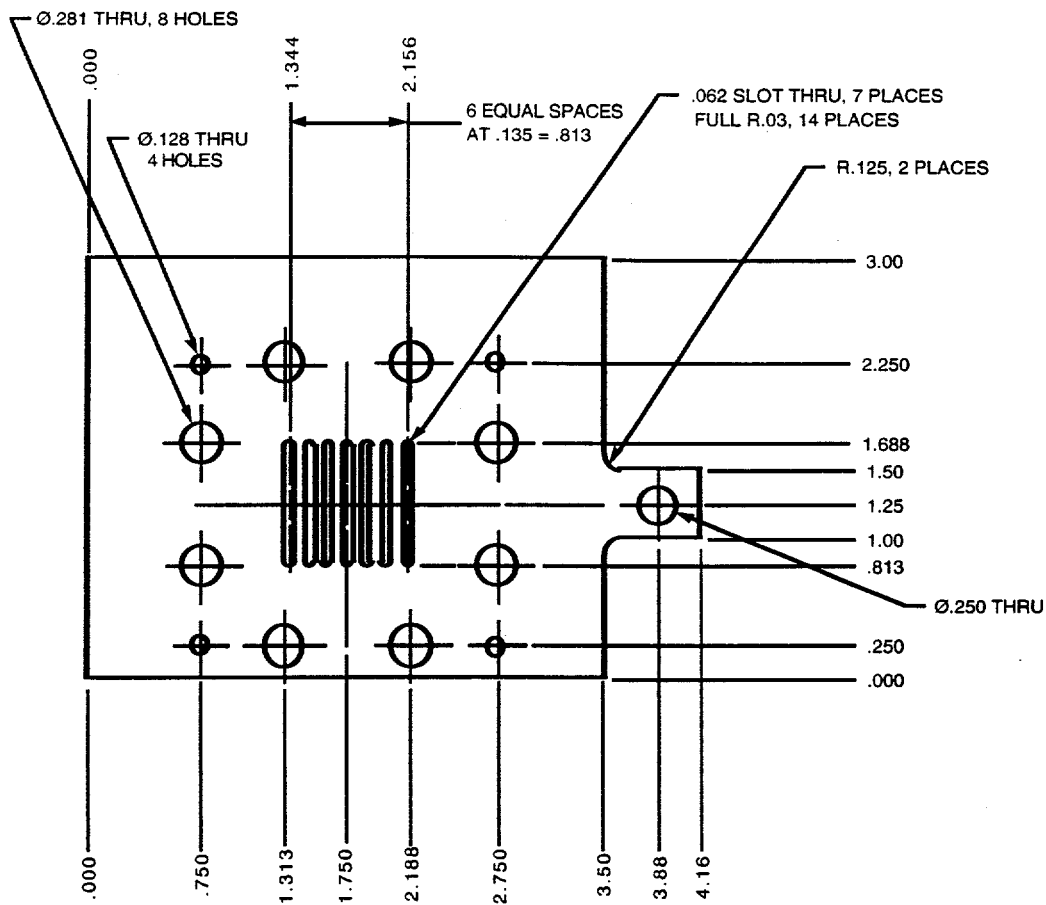




NOTE: USE TEMPLATE TO CUT ALL GASKETS. USE NO. 4 CORKBORE OR SHARP KNIFE TO CUT HOLES.  
 USE TEMPLATE TO CUT MEMBRANE/ELECTRODE ASSEMBLY. DO NOT CUT OUT CENTER SQUARE  
 IN M&E. EXTREME CARE MUST BE USED IN CUTTING HOLES TO PREVENT TEARING OF MEMBRANE.

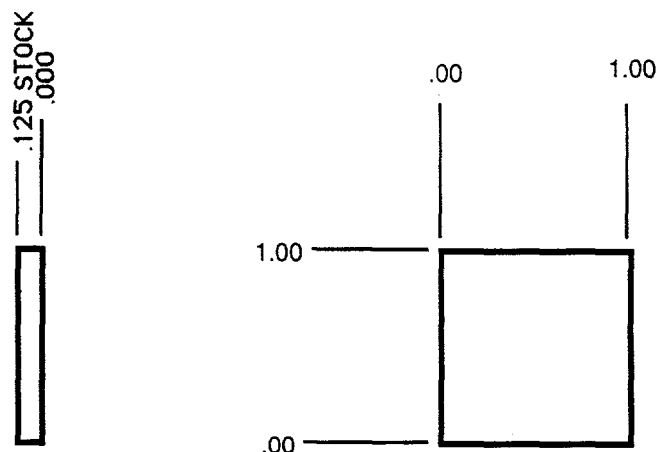
SCALE: 1/1, MAT'L: PLEXIGLAS (PMMA), QTY: 1 EACH

Figure 7: Electrolyzer Gasket Template



SCALE: 1/1, MAT'L: SS 316L, .047 THICK, QTY: 2 EACH

Figure 8: Electrolyzer Current Collector



SCALE: 1/1, MAT'L: PLEXIGLAS (PMMA), QTY: 1 EACH

Figure 9: Electrolyzer Carbon Paper Template

#### Pressure Vessel Storage Unit:

The hydrogen is stored in a pressure vessel equipped with a pressure gauge. Hydrogen production can then be determined from the known volume and pressure. Suitable materials for the pressure vessel include aluminum or 316 stainless steel. The pressure vessel and all tubing, connectors and valves used in the system must be rated to withstand the maximum working pressure, which is 100 psig in this experiment. The oxygen side of the electrolyzer is run at atmospheric pressure.

The electrolyzer can withstand pressures of several hundred psi across the membrane. As hydrogen is generated in the fixed volume of the cell, tubing and storage vessel the pressure of the hydrogen will increase. In this way the electrolyzer serves as a pump to pressurize the hydrogen for storage. The pressure relief valves insure that the maximum working pressure is not exceeded. A pump-out valve is needed to purge the hydrogen lines and the pressure vessel prior to the start of the experiment. This valve is also used to vent the system when the experiment is concluded. A second valve can be used to isolate the pressure vessel from the tubing if so desired.

#### System Assembly:

Insulated copper wires are used to connect the output from the photovoltaic array to the current collectors. The positive lead is connected to the gold plated anode current collector and the negative lead to the cathode current collector. The hydrogen tubing is used to connect the hydrogen side of the electrolyzer

with the storage vessel and the pump out valve as shown in Figure 1. The oxygen and the hydrogen side of the electrolyzer, all tubing connections, and the pressure vessel must all be leak tested to ensure that they are leak tight prior to operation.

### Experimental Procedure:

By filling with known volumes of water make calibration marks on the side on the anode and cathode water chambers. These marks will be used to determine the volume of water electrolyzed. The experiment should be concluded when the water level drops below the bottom of the top chamber in the anode end plate to ensure that the membrane does not dry out.

The anode and cathode water chambers are filled with distilled water. The hydrogen tubing and storage vessel are purged by pumping and backfilling with an inert gas, such as nitrogen, to remove the air. Be careful as excess pumping will evaporate the water in the cathode chamber. If the hydrogen is to be vented pumping is not necessary.

A plastic tube can be attached to the cathode port and used to vent the hydrogen generated by bubbling it through a beaker of water. One multimeter is used to measure the current from the photovoltaic array and another is used to measure the voltage across the current collectors. The control rheostat is set to zero or the open position and the electrical connections are then made to the current collector plates.

The minimum voltage required to separate water can be calculated from the difference in the enthalpy of the initial state (liquid  $H_2O$ ) and the final state (gaseous  $H_2$  and  $O_2$ ). This is called the enthalpy of formation. The formula is:

$$E = - \Delta H_f / (n F) \quad (1)$$

where  $\Delta H_f$  is the enthalpy of formation for liquid water, -68,317 Cal/gm mole,  $n$  is the number of electrons, 2 in our case, and  $F$  is the Faraday constant, 96,491 coulombs/mole. Using these numbers the minimum required voltage is calculated to be 1.48 volts. This is the voltage which would be required in a system with zero losses. In all real systems there are losses, so the required voltage is larger. These losses or additional voltage drops include the internal and interfacial resistances of the components used in the electrolyzer. Until the applied voltage is large enough to overcome the sum of 1.48 volts and all losses electrolysis will not take place. Increase the power slowly using the control rheostat until bubbles are observed when looking through the plexiglass housing. Record the voltage at which bubbles were first observed. How large is this voltage compared to the minimum required voltage of 1.48 volts? The ratio

of actual voltage to minimum voltage is called the voltage efficiency of the electrolyzer. How efficient is the electrolyzer?

$$\text{Voltage Efficiency} = 1.48 \text{ V} / \text{measured V} \quad (2)$$

The hydrogen output of the electrolyzer is proportional to the current flow. Adjust the rheostat until a steady reaction is taking place. Monitor the current flow through the electrolyzer. Record the water levels in both the anode and cathode chambers and measure the change in water volume over a known time period. (During electrolysis a significant volume of water will travel through the membrane, so the volume of water in both chambers must be used to determine the amount of water electrolyzed.) Using the density of water and the reaction equations calculate the amount of water that should be electrolyzed by the measured current in the time period. Compare this volume with your measured volume of water usage. The ratio of the actual hydrogen produced to the theoretical amount is called the current efficiency of the electrolyzer. The theoretical amount of hydrogen produced can be calculated by using the measured current and time:

$$N_{H_2} = I t / (F n) \quad (3)$$

where  $N_{H_2}$  is the number of moles of  $H_2$  produced,  $I$  is the current in A,  $t$  is the time in seconds, and  $F$  and  $n$  are as defined above. Since we know from figure 4 that 1 mole of  $H_2O$  should produce 1 mole of  $H_2$  we can compare the amount of water electrolyzed to the amount of hydrogen which should be produced as calculated by equation 3.

The amount of hydrogen generated can also be calculated by using the volume of the hydrogen gas produced and the final pressure of the hydrogen by using the ideal gas law:

$$N_{H_2} = P V / (R T) \quad (4)$$

where  $P$  is the gas pressure,  $V$  is the volume of the hydrogen,  $R$  is the gas constant,  $0.0821 \text{ (liter atm)/(mole K)}$ , and  $T$  is the temperature in Kelvin,  $K = C + 273.15$ .

The above procedures can be repeated with different settings of the control rheostat to examine the performance of the electrolyzer under different operating conditions.

**Acknowledgments:** The authors gratefully acknowledge the technical assistance of Mahlon S. Wilson, Chuck Derouin, Domenick DeCaro and Eric Baggs

of the Materials Science and Technology Division, Los Alamos National Laboratory for their assistance in design of the electrolyzer. Oliver Murphy, Lynntech, Inc.; Catherine Anderson, AeroVironment; and Pat Walters, TRW for their guidance on the electrolyzer and system design. W.L. Gore & Associates, Inc. for the catalyzed proton exchange membrane. Mary Georgeff-Daugherty for solar array assembly. Fred Edeskuty for hydrogen safety advice. Marcia Zalbowitz for project coordination.

#### **Notes to the Instructor:**

The Compressed Gas Association, Inc. is located at 1725 Jefferson Davis Highway, Suite 1004, Arlington, VA 22202-4100, (703) 979-0900.

The National Fire Protection Association (NFPA) is located at 1 Batterymarch Park, P.O. Box 9101, Quincy, MA 02269-9101.

Carbon paper can be obtained from Spectracorp, 599 Canal Street, Lawrence, MA 01840, (508) 682-1232.

Reinforced Silicone gasket material can be obtained from CHR Industries, Inc., 407 East Street, PO Box 1911, New Haven, CT 06509-9988, (203) 777-3631.

#### **References:**

1. Hydrogen, CGA G-5-1991, Compressed Gas Association, Inc.
2. Standard for Hydrogen Piping Systems at Consumer Locations, CGA G-5.4-1992, Compressed Gas Association, Inc.
3. Standard for Gaseous Hydrogen Systems at Consumer Sites, NFPA 50A, 1994.
4. Hydrogen Safety, An Annotated Bibliography of Regulations, Standards and Guidelines, J. Hord, Hydrogen Energy System, Proc. World Hydrogen Energy Conf., Zurich, Switzerland, Aug. 21-24, 1978, Vol. 4, T.N. Veziroglu and W. Seifritz, Editors, Pergamon Press Inc., Elmsford, N.Y.

# **Why Hydrogen?**

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- The output of renewable energy sources can vary depending on weather conditions.
- Hydrogen can serve as both an energy storage means and an energy carrier in renewable energy systems.
- By using renewable sources to produce hydrogen, a fuel which can be stored and transported, a reliable and continuously available energy supply with a predictable long-term average output is created.



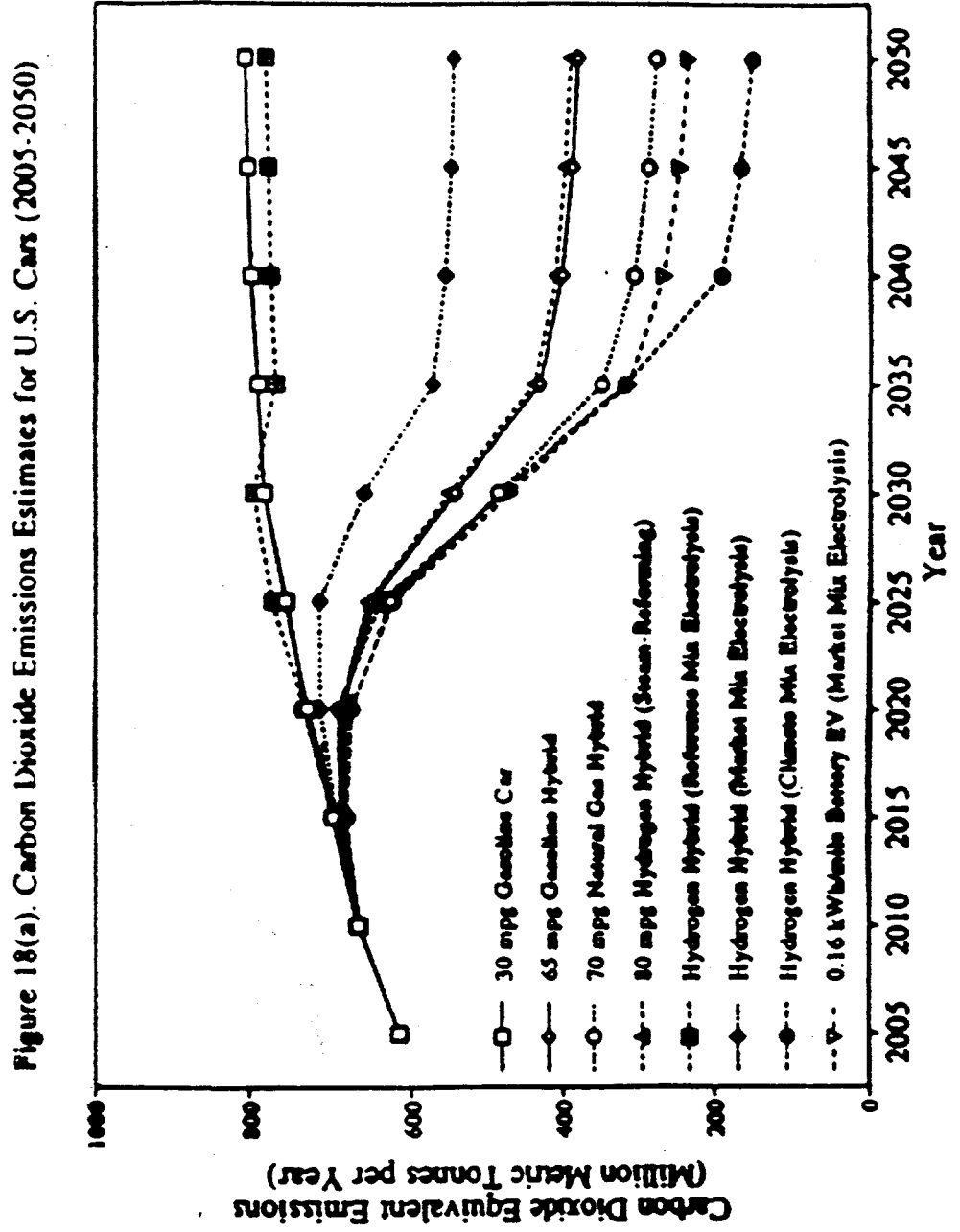
09/25/96

## **Strategic Overview: Program Perspective HTAP Vision**

- **Hydrogen will join electricity in the 21st century as the primary energy carriers in the Nation's sustainable energy future**
- **Hydrogen and electricity will ultimately come from renewable energy sources, although fossil fuels will provide a long-term transitional resource**
- **Future hydrogen suppliers will deliver a significant portion of America's energy for transportation and other applications**
- **For these applications, hydrogen offers a non-polluting, inexhaustible, efficient, and potentially cost-effective energy system derived entirely from domestic energy sources**



## Strategic Overview: Program perspective



## **This project has four main objectives.**

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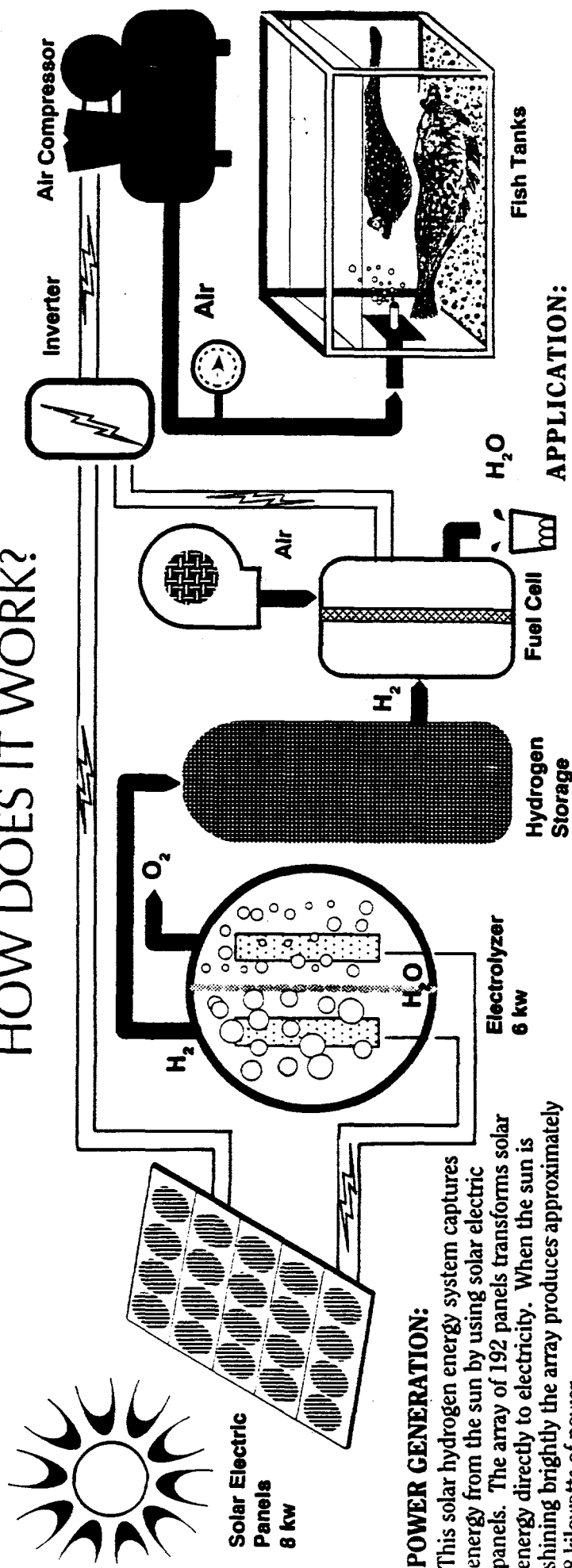
- **To expose students to the concept of fuel production using renewable sources.**
- **To build a small photovoltaic powered electrolyzer.**
- **To teach proper respect for hydrogen and oxygen safety requirements.**
- **To measure the efficiency of a single cell proton exchange membrane electrolyzer and develop a basic understanding of its operation.**

**Developers of solar hydrogen systems  
are excellent sources of information.**

- 
- **Humboldt State University, Arcata, CA**
  - **Clean Air Now/Xerox, El Segundo, CA**
  - **The Cooper Union, New York, NY**
  - **DLR - Institute for Technical Thermodynamics,  
Stuttgart, Germany**
  - **Helsinki University of Technology, Espoo,  
Finland**
  - **King Abdulaziz University, Chemical and  
Materials Engineering Department, Jeddah,  
Saudi Arabia**
- 

**Los Alamos**

# HOW DOES IT WORK?



## POWER GENERATION:

This solar hydrogen energy system captures energy from the sun by using solar electric panels. The array of 192 panels transforms solar energy directly to electricity. When the sun is shining brightly the array produces approximately 8 kilowatts of power.

## GAS GENERATION AND STORAGE:

The electrolyzer uses the electricity to split water into hydrogen ( $H_2$ ) and oxygen ( $O_2$ ). The hydrogen gas is collected and stored in three 500 gallon tanks behind the lab at a pressure of 100 pounds per square inch. The oxygen gas is vented to the atmosphere.

At the maximum hydrogen production rate of 24 standard liters per minute, the electrolyzer consumes 1 liter of water per hour.

## APPLICATION:

The electricity from this system is used to power the air compressor that aerates the aquaria in the Marine Lab. Except on the darkest of days, the array produces more than enough electricity during daylight hours to run the compressor directly. Any extra power is used to run the electrolyzer.

In this way water and sunlight, both natural and abundant, are used in a cycle to produce power. And because hydrogen stores solar energy, the power is available whenever it is needed.

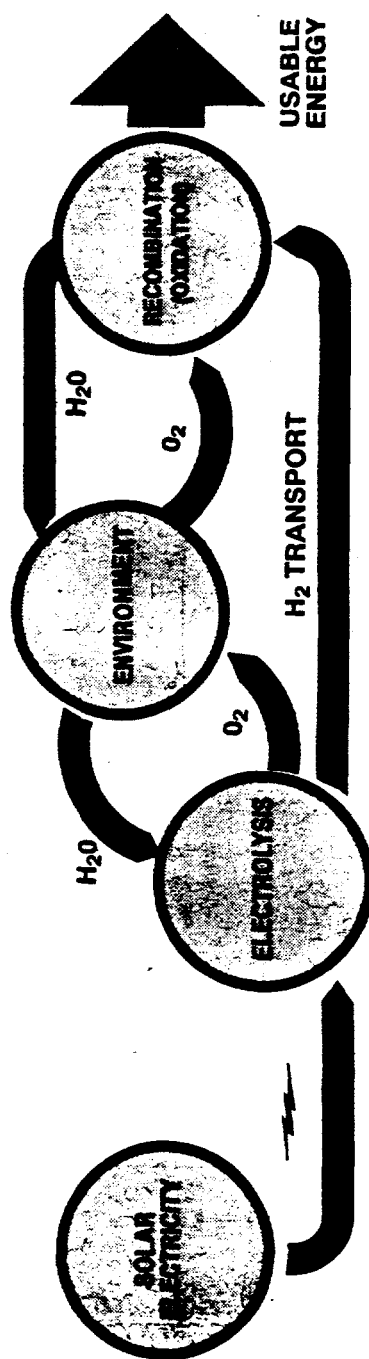
## REGENERATION:

At night or when the clouds are thick, the system automatically shifts to fuel cell operation. The fuel cell directly converts chemical energy into electrical energy by combining the stored hydrogen with oxygen from the air.

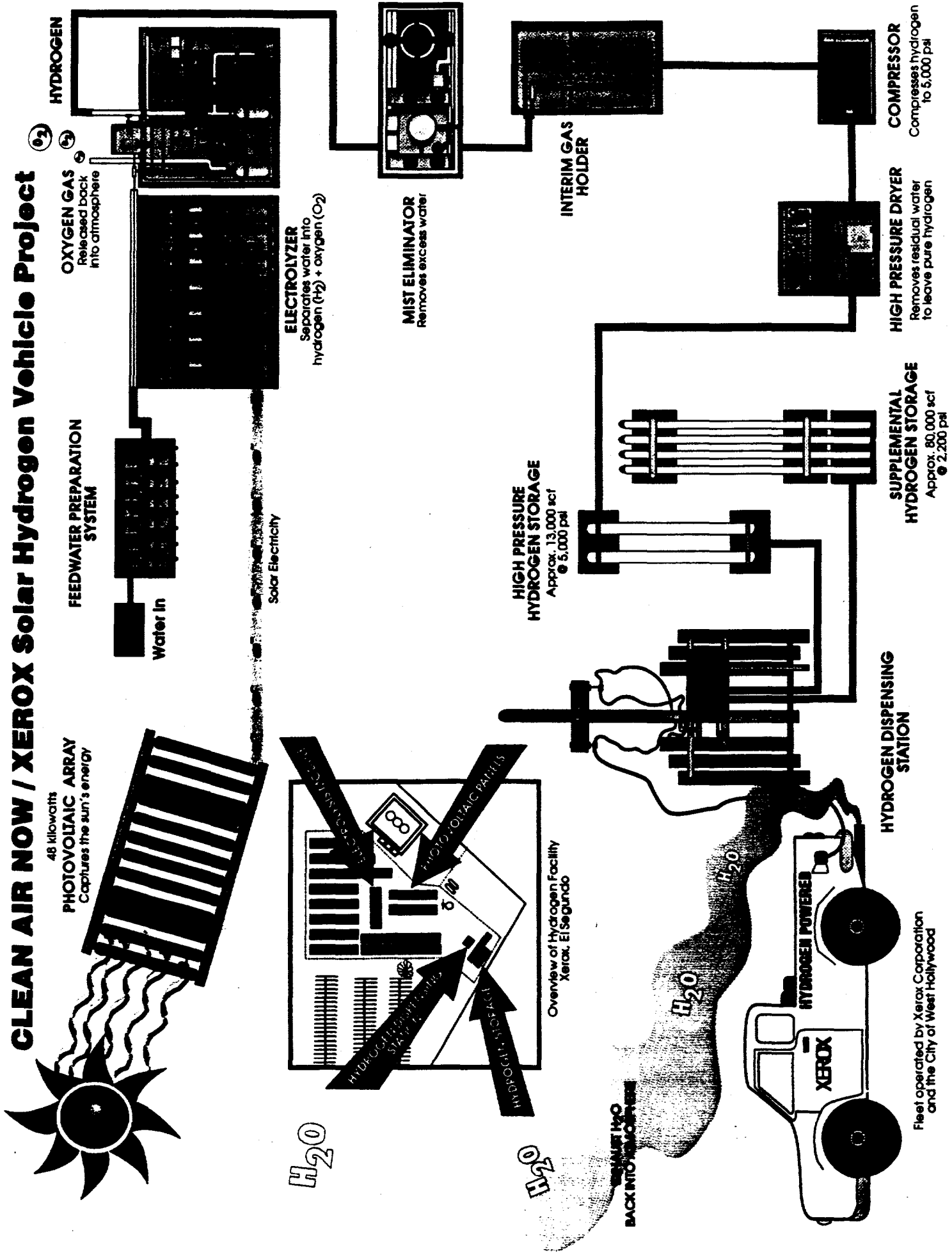
A fuel cell is similar to a battery, except that a battery requires recharging when it runs down. The fuel cell continues to produce power as long as it is fed hydrogen and air.

## THE SOLAR HYDROGEN CYCLE:

In the solar hydrogen cycle, solar energy provides the electricity to remove hydrogen from ordinary water by the process of electrolysis. The hydrogen may then be stored or transported. When hydrogen is recombined with oxygen, usable energy results. No resources are consumed and the only byproduct is pure water. In this cycle hydrogen is an energy carrier; it allows us to store and transport solar energy in large quantities.



# CLEAN AIR NOW / XEROX Solar Hydrogen Vehicle Project

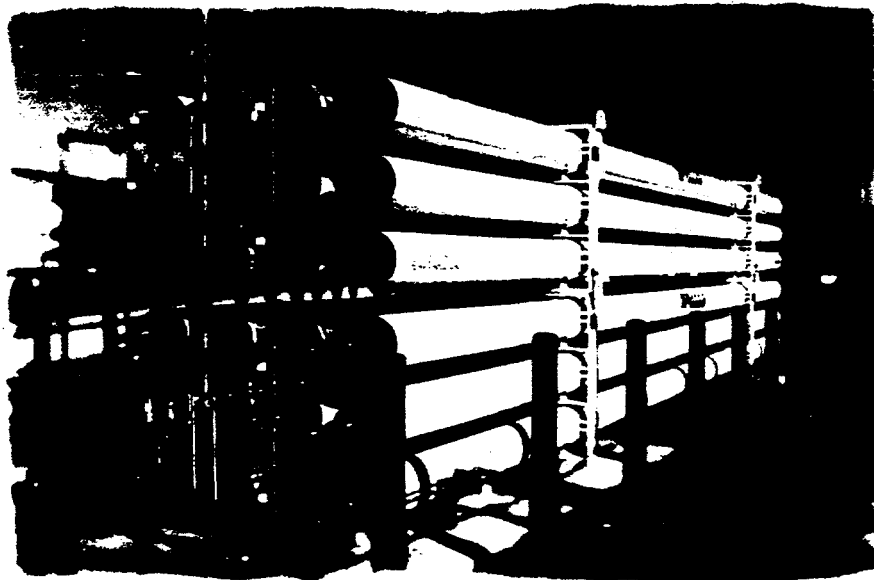


Fleet operated by Xerox Corporation and the City of West Hollywood

**CLEAN AIR NOW SOLAR HYDROGEN REFUELING STATION  
XEROX FACILITY - EL SEGUNDO, CA (DECEMBER 1994)**

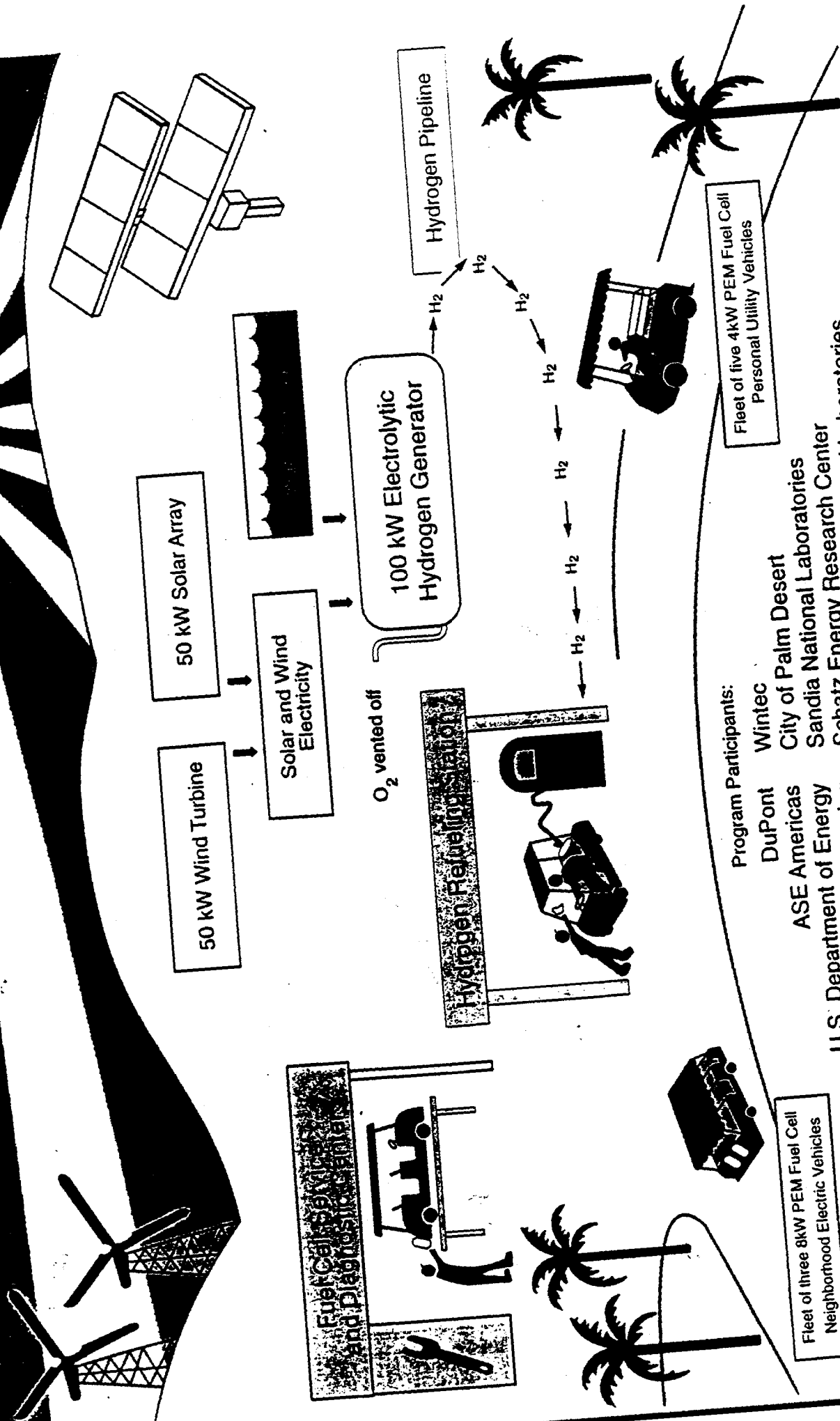


**REFUELING THE BALLARD TECHNOLOGIES FUEL CELL BUS, WHILE IT WAS ON  
DEMONSTRATION RUNS AT THE LOS ANGELES INTERNATIONAL AIRPORT.**



**SUPPLEMENTAL (2200PSI) HYDROGEN STORAGE TANKS SUPPLIED BY PRAXAIR, INC**

# Renewable Hydrogen Transportation System for the City of Palm Desert, California



## Program Participants:

DuPont  
ASE Americas  
U.S. Department of Energy  
Teledyne Brown Engineering  
South Coast Air Quality Management District

Wintec  
City of Palm Desert  
Sandia National Laboratories  
Schatz Energy Research Center  
Lawrence Livermore National Laboratories

## **Safety is an essential component of any hydrogen project.**

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- **Why is safety important : 1) protection of personnel, 2) protection of equipment, and 3) development of advanced technology depends on public acceptance.**
- **Following established guidelines and procedures is especially critical for those working with hydrogen and oxygen for the first time.**
- **Students must be taught proper safety procedures before they operate a system.**



### Combustion Properties<sup>a</sup> of Hydrogen, Methane, and Gasoline

<u>Property</u>	<u>Hydrogen</u>	<u>Methane</u>	<u>Gasoline</u>
Flammability Limits (Vol %)	4.0 to 75.0	5.3 to 15.0	1.0 to 7.6
Detonability Limits (Vol %)	18.3 to 59 <sup>b</sup>	6.3 to 13.5	1.1 to 3.3
Minimum Ignition Energy (mJ)	0.02	0.29	0.24
Autoignition Temperature <sup>c</sup> (K)	793 to 1023	903 to 1493	501 to 744
Flame Temperature (K)	2318	2148	2470
Burning Velocity (cm/s)	265 to 325	37 to 45	37 to 43
Detonation Velocity (km/s)	1.48 to 2.15	1.39 to 1.64	1.4 to 1.7
Diffusion Velocity (cm/s)	< 2.0	< 0.51	< 0.17
Buoyant Velocity (m/s)	1.2 to 9	0.8 to 6	Nonbuoyant
Quenching Gap (mm)	0.64	2.03	2.0
Maximum Experimental Safe Gap (mm)	0.08	1.2	0.7
Stoichiometric Composition (%) <sup>a</sup>	29.53	9.48	1.76

<sup>a</sup> In mixtures with air at conditions of 0.101325 MPa (1 atmosphere) and 294 K (70°F).

<sup>b</sup> For low energy initiation. <sup>c</sup> A range is necessary for this value because the autoignition temperature depends upon the ignition method.

Figure 39

**Hydrogen embrittlement lowers the ductility and strength of many structural materials.**

---

- **Hydrogen reaction embrittlement - a chemical process, typically at temperatures above 500K.**
- **Internal embrittlement- hydrogen introduced in the production of the metal.**
- **Environmental embrittlement- hydrogen introduced from the environment.**

**Minimum Ignition Temperature of Selected Plastics and Elastomers in Oxygen at One Atmosphere Pressure**

Material	Minimum Ignition Temp (K)
Polyimide (Vespel)	773
Chlorotrifluoroethylene (TFE)	773
Tetrafluoroethylene (TFE)	773
Duroid 5600	741
Duroid 5813	736
Duroid 5870	725
Duroid 5650	717
Rulon A	736
Rulon B	733
Rulon C	731
Graphite Asbestos	733
Polymethylmethacrylate (Plexiglas) ×	703
TFE (carbon filled)	693
Fluorinated ethylene propylene copolymer (FEP)	685
Silicone rubber	663
Kel-F 5500	613 to 625
Kel-F 3700	605 to 614
Carbon	603
Fluorosilicone	593
Polyvinylchloride	663
Nylon <sup>a</sup>	618
Mylar <sup>a</sup>	593
Butyl rubber <sup>a</sup>	548
Neoprene <sup>a</sup>	523 to 543
Polyethylene <sup>a</sup>	433 to 493
Natural rubber <sup>a</sup>	423

<sup>a</sup> Not recommended for oxygen service, included for comparison only.

Figure 57

## Combustion Rate for Metal Rods in Oxygen at One Atmosphere Pressure

Material <sup>a</sup>	<u>Combustion Rate (cm/s)</u>		
	<u>Up</u>	<u>Down</u>	<u>Horizontal</u>
Mild Steel	0.76	1.27	1.10
Aluminum	25.4	----	----
309 Stainless Steel	----	0.43	0.97
316 Stainless Steel	2.03	----	0.76
316L Stainless Steel	0.18	----	----
410 Stainless Steel	0.13	----	0.61
17-4PH Stainless Steel	0.30	----	0.76
4140 Stainless Steel	0.33	----	0.15
Nickel <sup>b</sup>	none	----	none
Monel <sup>b</sup>	none	----	none
Inconel <sup>b</sup>	none	----	none
Bronze <sup>b</sup>	none	----	none
Hastelloy	0.15	----	0.20

<sup>a</sup> Rods 1.59 mm (1/16th in.) to 4.76 mm (3/16th in.) diameter.

<sup>b</sup> These materials did not propagate combustion in one-atmosphere oxygen.

Figure 56

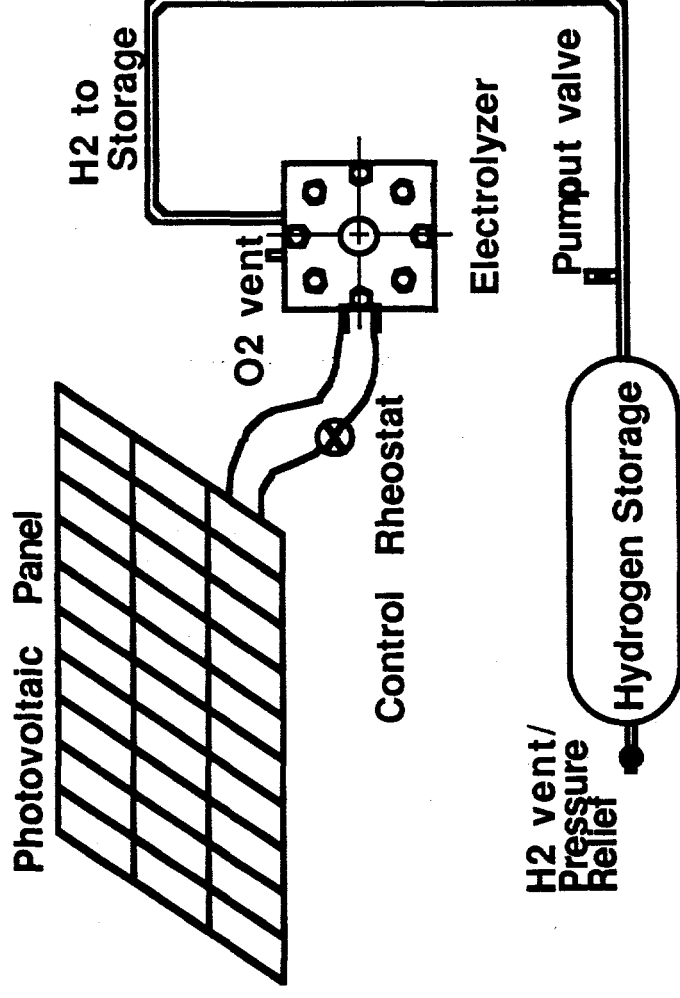
## Combustion Rate of Selected Non-Metals in Oxygen

Material	Combustion Rate (cm/s) in Exposure of		
	21 % O <sub>2</sub> , 1 Atm	100 % O <sub>2</sub> , 0.2 Atm	100 % O <sub>2</sub> , 1 Atm
Cotton	6.35	2.54	18.80
Dacron	1.78	2.29	5.84
Epoxy	----	----	0.30
Neoprene	----	0.25	1.02
Nomex	1.32	0.79	2.44
Nylon (fabric)	0.81	1.17	2.59
Polyethylene	----	0.15	0.69
PVC	----	0.76	2.54
Polyurethane	----	1.42	1.78
Silicone	----	0.51	2.79
Velcro	----	0.61	1.22

Figure 59

**The photovoltaic panel provides power to the electrolyzer which produces the hydrogen from water.**

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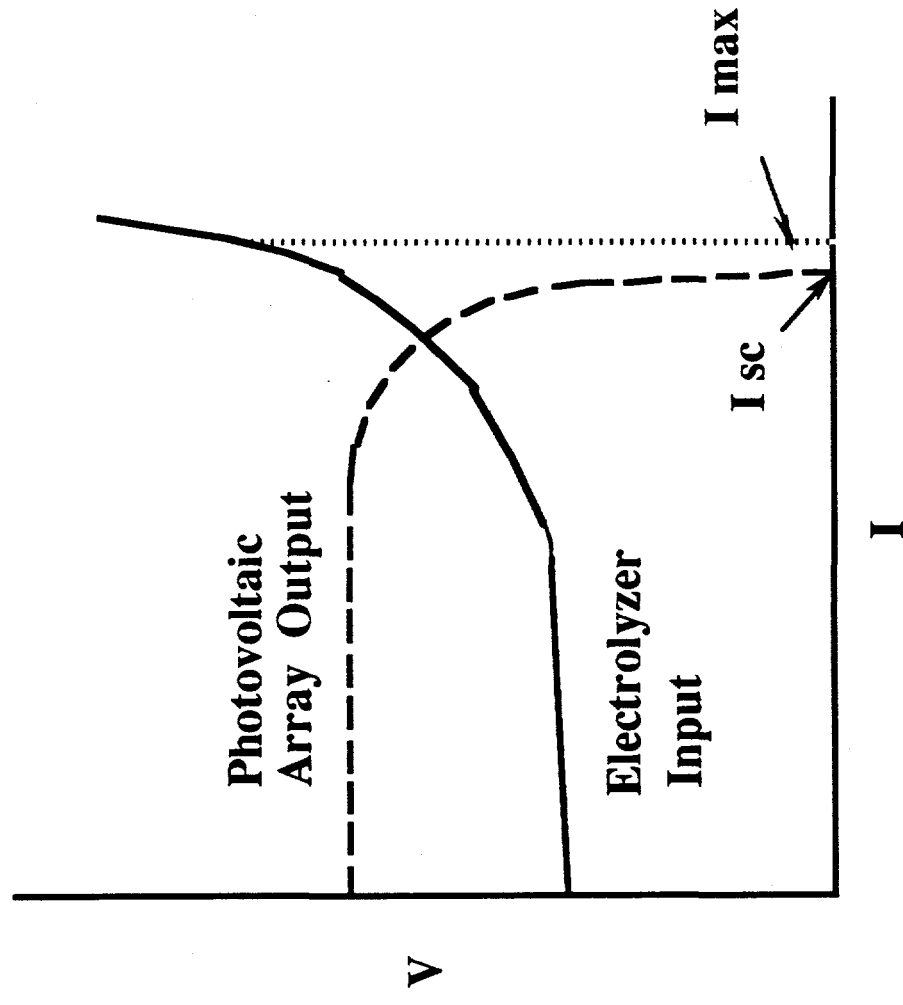
**Solar cells are stacked in series to give the required voltage and in parallel to provide the required current.**

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- 56 cells were used in the array, 7 in series for an open circuit voltage of 3.75 V, 8 strings in parallel for a nominal current of 1.6 A
- Cells are brittle and require careful handling.
- 3 mil copper foil was used to connect individual cells.
- Fixtures to bend the foil and hold the cells during soldering are very helpful.
- Solar cells are available.

**The maximum short circuit current of the solar array is less than the maximum operating current of the electrolyzer.**

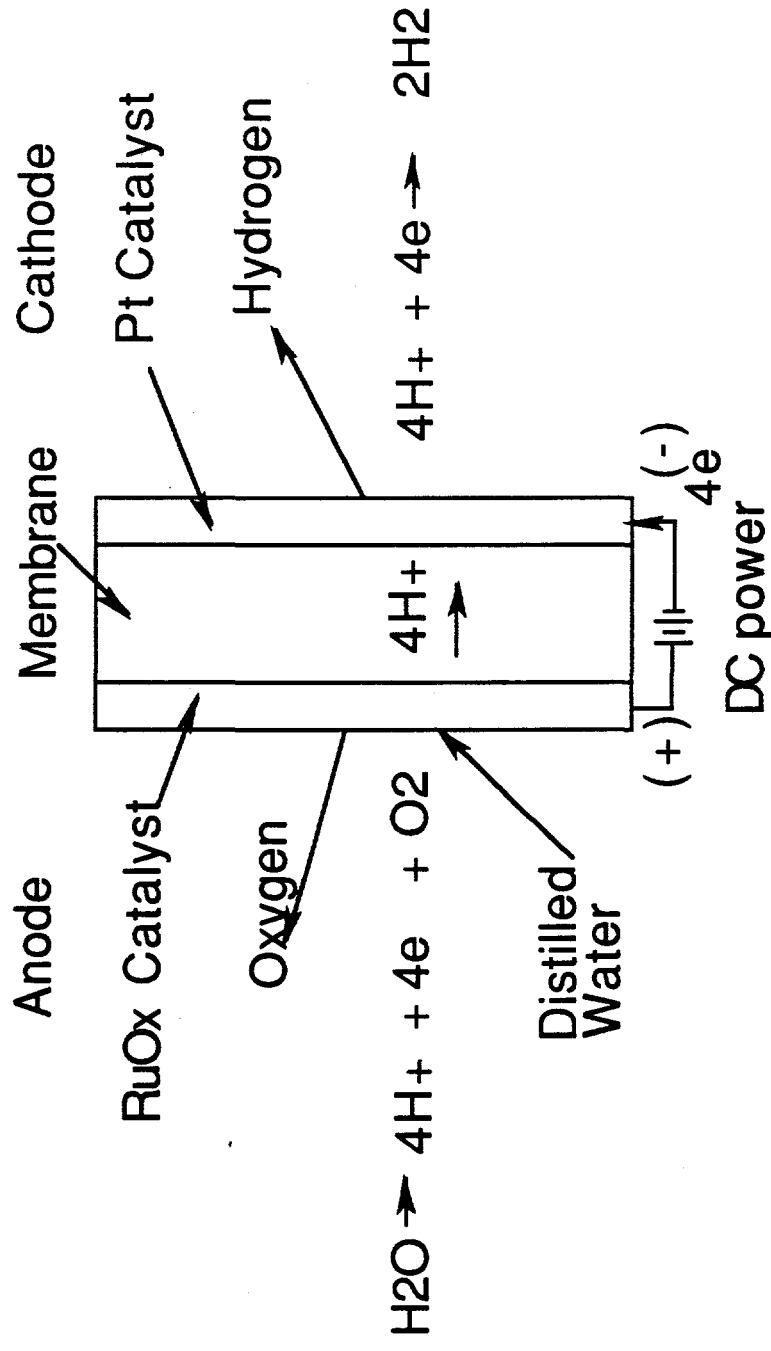
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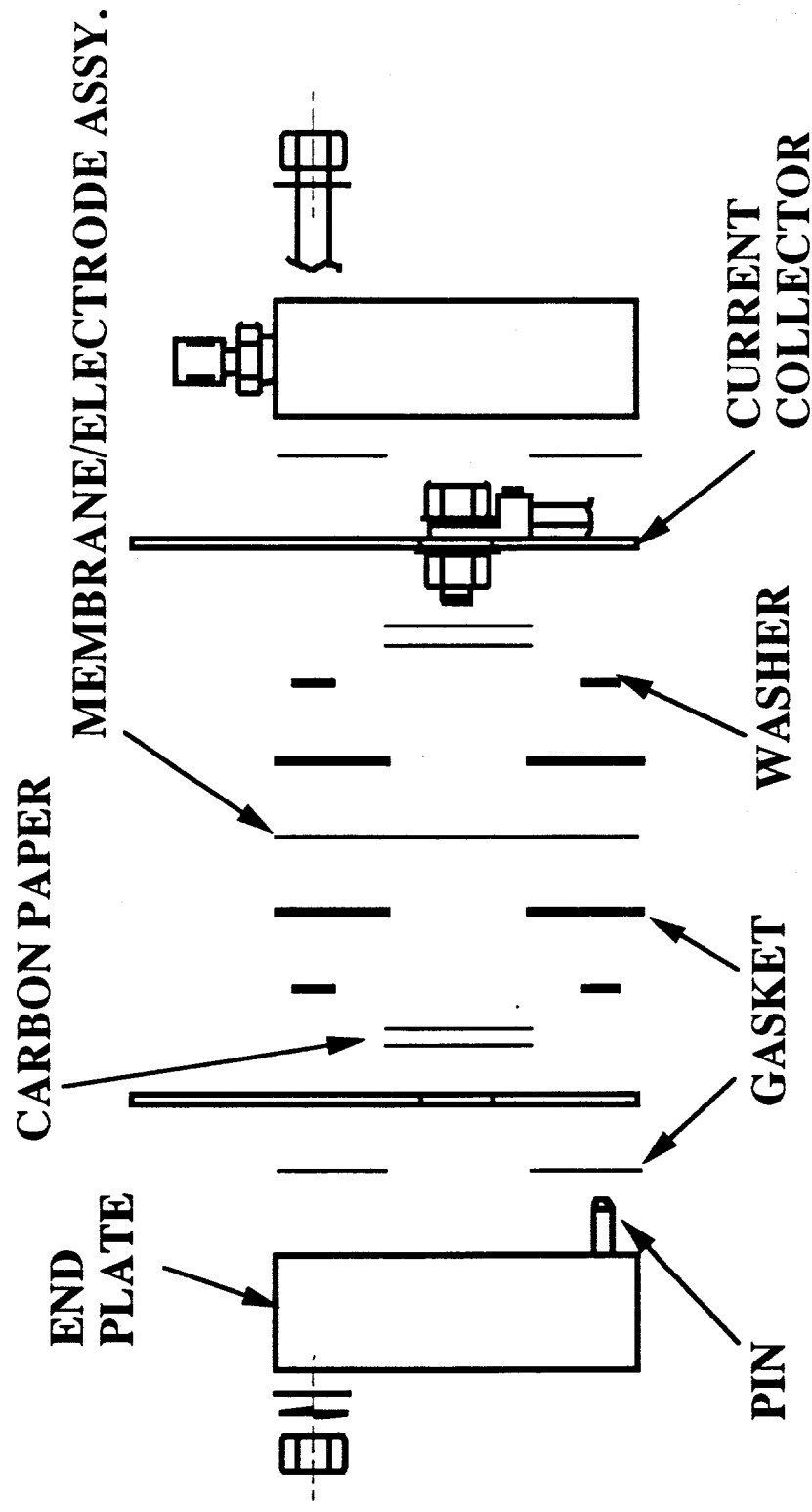


**This electrolyzer is built around the proton conducting polymer-electrolyte membrane.**

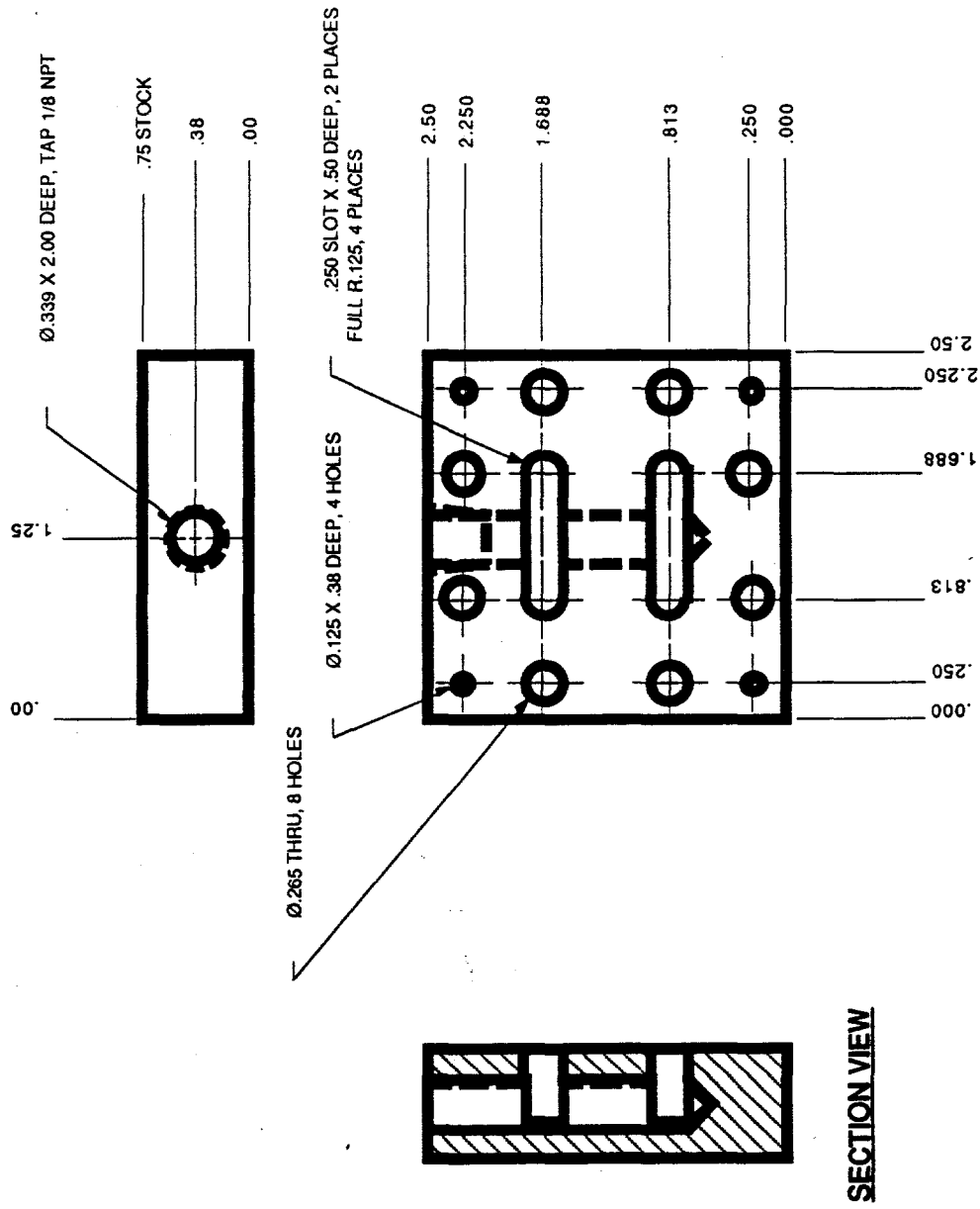
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**The electrolyzer is built symmetrically  
from each side of the membrane.**



The plexiglas end plates provide mechanical support and contain water, oxygen and hydrogen flow passages.

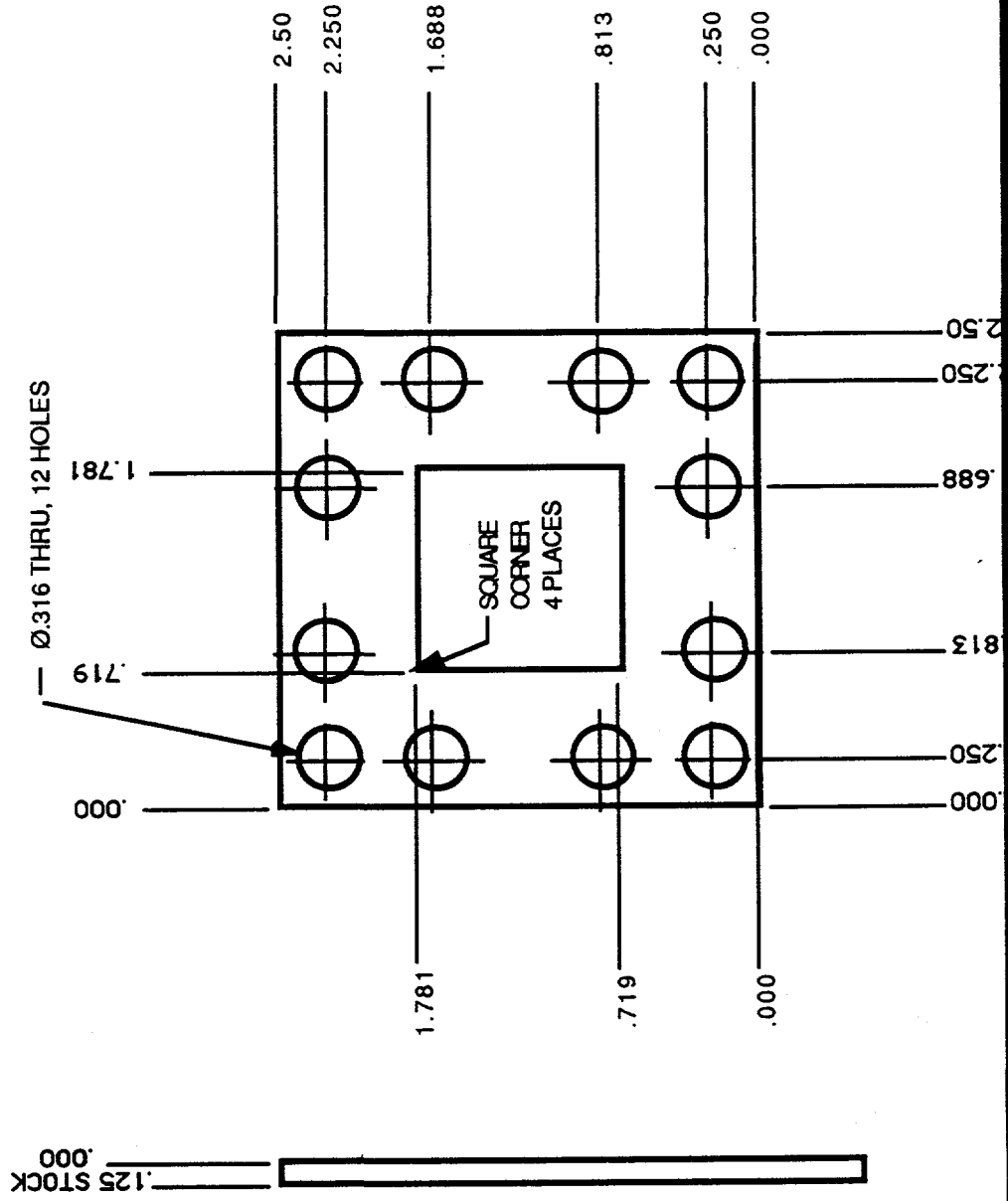


Los Alamos

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# Los Alamos

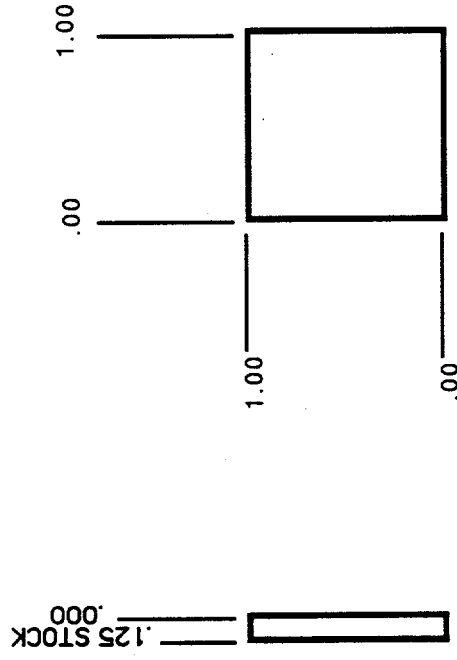
The same template is used to cut the gaskets  
and the membrane/electrode assembly.



Los Alamos

**The carbon paper provides a cushioned  
conductive support between the current  
collector and the membrane electrode assembly.**

---



SCALE: 1/1, MAT'L: PLEXIGLAS (PMMA), QTY: 1 EACH

---

**Los Alamos**

## **A pressure vessel can be used to store the hydrogen produced.**

---

- The pressure vessel and all tubing, connectors and valves used in the system must be rated to withstand the maximum working pressure, 100 psig.
- A pressure relief valve is required to insure that the maximum working pressure is not exceeded.
- A pump-out valve is needed to evacuate the hydrogen lines and the pressure vessel prior to the start of the experiment.
- Suitable materials for the pressure vessel include aluminum or 316 stainless steel.

## **System Assembly**

---

- The positive lead from the photovoltaic array is connected to the gold plated anode current collector.
- The negative lead is connected to the cathode current collector.
- The hydrogen tubing is used to connect the hydrogen side of the electrolyzer with the storage vessel.
- The oxygen and the hydrogen side of the electrolyzer, all tubing connections, and the pressure vessel must all be leak tested to ensure that they are leak tight prior to operation.



## **System Operation**

---

- Review basic hydrogen and oxygen safety with system operators.
- Set up the system on a stable surface away from any ignition sources.
- Fill the anode and cathode water chambers with deionized water.
- Ensure that hydrogen and oxygen vents are separated, evacuate the storage vessel and connecting lines if the hydrogen is stored.
- Apply power from the solar array.

## Ideas for Experiments

---

- Determine the voltage at which electrolysis starts and compare to the ideal voltage. Calculate the efficiency of the system by:  $v_{\text{reversible}}/v_{\text{actual}}$  ( $v_{\text{reversible}} = 1.48 \text{ V}$ )
- Measure the current and the amount of water consumed for a given time period. Calculate hydrogen production using both measurements and compare.
- Use the pressure and volume of a storage vessel to calculate the amount of hydrogen produced and compare to the above calculations.

## **Summary**

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- This system can provide a wonderful introduction to renewable hydrogen production.
- Hydrogen can be used to run a fuel cell producing electricity and water, thus completing a sustainable zero pollution energy cycle.
- Hydrogen is a fuel, please ensure proper safety procedures are followed at all times.

---

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>Materials for Hydride-Based Batteries  
>R. B. Schwarz  
>Center for Materials Science  
>Los Alamos National Laboratory, Los Alamos, NM 87545

>

>Until recently, apart from the lead-acid battery, the nickel/cadmium battery  
>had the lion's share of the rechargeable electrochemical energy storage system  
>market. Because of environmental concerns related to the toxicity of  
>cadmium, the cadmium electrode is being replaced by the metal hydride  
>electrode. Nickel/metal hydride batteries have an additional advantage of a  
>slightly higher energy density storage.

>The positive nickel hydroxide electrode, common to both the nickel/cadmium  
>and the nickel/metal hydride electrode, has been studied for many years and  
>is the positive electrode of choice in most batteries. The consensus is  
>that little can be done to improve the nickel electrode. The metal hydride  
>electrode, however, requires further study and improvement. In the  
>nickel/metal hydride battery, the metal hydride electrode operates in  
>concentrated KOH. The main problem with this electrode relates to the loss  
>of hydrogen storage capacity with cyclic hydrogen charging/discharging  
>which is thought to be caused by the corrosion of the hydride material in  
>the KOH. The workshop will review the fundamentals of the hydride battery  
>and the current efforts at Los Alamos and elsewhere for improving the  
>performance of the metal hydride electrode.

>=====

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# MATERIALS FOR HYDROGEN-BASED BATTERIES

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## Key Words

Batteries, Hydrogen batteries, Hydrides, Alloys, Energy Storage

## Prerequisite Knowledge

Basic materials science (alloy synthesis), x-ray diffraction

## Objective

To demonstrate the use of metal hydrides in the storage of hydrogen, in particular for the manufacture of nickel/metal hydride batteries. To illustrate the construction, testing, and performance of nickel/metal hydride batteries. To discuss the problems in optimizing the performance of nickel/metal hydride batteries.

## Equipment

The participants will be shown first hand the operation of ball mills for alloy powder synthesis; glove boxes for handling metal powders to prevent air contamination; x-ray diffractometers for studying the structure of alloys; differential scanning calorimeters for studying the thermal stability and transformations in alloys; Sieverts apparatus for measuring the hydrogen (gas) absorption/desorption characteristics of metallic powders; and a battery tester to test the performance of electrodes fabricated in the laboratory when operating in concentrated KOH as part of a rechargeable battery.

## Introduction

Currently, the nickel/cadmium batteries have the largest share of the rechargeable battery market. Applications for these batteries are for aircraft, military and defense, telecommunications, home-use portable devices (photography, portable phones, portable computers, camcorders, power tools, toys), and standby power (emergency lighting, alarms). Incentive for developing nickel/metal hydride (Ni-MH) batteries comes from pressing health and environmental concerns to find replacements for the nickel/cadmium rechargeable batteries. Due to worker's safety requirements, processing of cadmium for batteries in the U.S. is already in the process of being phased out. Furthermore, environmental legislation for the 1990's and the 21st century will most likely make it imperative to curtail the use of cadmium in batteries for consumer use. In spite of these pressures, next to the lead-acid battery, the nickel/cadmium battery still has the largest share of the rechargeable battery market. Further incentives for researching hydrogen-based batteries comes from the general belief (e.g., Draft of the DOE "Hydrogen Implementation Plan, FY 1994-1998") that hydrogen and electricity will displace and eventually replace a significant fraction of the energy-carrying contributions of fossil-fuel resources, becoming the foundation for a sustainable energy system based on renewable sources. Finally, there is considerable interest in the development of Ni-MH batteries for electric vehicles and hybrid vehicles.

The development of a high-rate, long cyclic life, Ni-MH battery would give American business a competitive advantage over foreign manufacturers, would provide the military and business an alternative to an environmentally hazardous power source, and would

increase the probability of successfully developing a battery for a hybrid vehicle in support of the Partnership for a New Generation of Vehicles (PNGV).

### Why use hydrogen?

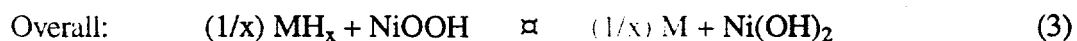
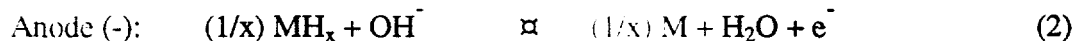
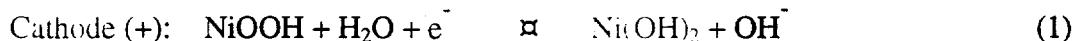
The ability of hydrogen to react with various metals and form hydrides (metal-hydrogen compounds) opens the possibility of using hydrides in the manufacture of rechargeable batteries. On earth there is almost no free molecular hydrogen. Hydrogen gas, however, can be easily made from readily available materials, e.g., by the electrolysis of water. Once made, hydrogen can be stored in various forms (gas, liquid, hydrides). At atmospheric pressure, 1 gram of molecular hydrogen gas occupies a volume of about 22 liters and thus the storage of hydrogen in gas form is inefficient, unless the gas is pressurized to several hundred atmospheres and kept in a strong pressure vessel. The storage of hydrogen in liquid form requires cooling the gas and its container to cryogenic temperatures (about 20 Kelvin), and keeping them at that temperature. It is thus clear that neither form of storage is suitable for common everyday use. In contrast, the storage of hydrogen in hydride form is both economical and safe for many applications.

Hydrogen reacts with many elements to form compounds. Of these, the transition metals (Groups IIIA through VIIIA in the periodic table, including the lanthanides and actinides) are most important because they can absorb large quantities of hydrogen and form metallic hydrides. Metallic hydrides exhibit the general properties of metals, i.e., high electrical and thermal conductivity, hardness, and metallic luster.

During the last five years, Ni-MH batteries have entered the international market as replacements for nickel-cadmium (Ni-Cd) batteries. The nickel/metal hydride battery is very similar to the nickel/cadmium battery but with significant advantages over the latter. The nickel/metal hydride battery has a 20% to 30% higher specific energy density (gravimetric as well as volumetric) than a comparable nickel/cadmium cell while maintaining the same electrical (similar open-circuit potential) and mechanical characteristics. Another advantage of the nickel/metal hydride battery is that it has no 'memory effect' i.e., it does not have to be completely discharged to be completely charged anew. On drawback of the Ni-MH batteries, however, is a somewhat poorer high-rate power delivery.

### Fundamental Properties of Nickel/Metal hydride Batteries

The nickel/metal hydride battery operates in concentrated KOH electrolyte. The electrode reactions in a nickel/metal hydride battery are as follows:



The KOH electrolyte can only transport the  $\text{OH}^-$  ions and, to balance the charge transport, electrons must circulate through the external load, as shown schematically in figure 1. The nickel oxy-hydroxide electrode (equation 1) has been extensively researched and characterized, and its application has been widely demonstrated for both terrestrial and aerospace applications. Most of the current research in Ni/Metal Hydride batteries has as its purpose improving the performance of the metal hydride anode. Specifically, this requires the development of a hydride electrode with the following characteristics: (1) long cycle life, (2) high capacity, (3) high rate of charge and discharge at constant voltage, and (4) large retention capacity.

Of the 200 known hydrides of intermetallic compounds, only a few of them are good candidates for anode materials in KOH environments. The AB<sub>2</sub> Laves phases, of which ZrV<sub>2</sub> is a typical example, were discovered in 1966 and are the basis of the alloys developed by Ovonic Battery Company and licensed to companies in the U.S. and Japan [1]. The Haucke phase, LaNi<sub>5</sub>, was discovered at the Phillips Eindhoven Laboratories in 1970 and is one of the best materials for the reversible storage of hydrogen at near-ambient conditions. Electrochemical charging and discharging of LaNi<sub>5</sub> was demonstrated by Justi and co-workers in 1973. In recent years, research on the AB<sub>5</sub> alloys has concentrated on modifying the alloy composition by alloying with elements such as aluminum, tin, manganese, cobalt, silicon, chromium, and various rare-earth metals [2,3,4]. The purposes of these modifications have been to:

- (a) enhance the stability of the alloy, especially under cyclic charging/discharging
- (b) alter the 'plateau' pressures to enable the reversible charging at ambient conditions of pressure and temperature
- (c) increase the hydrogen storage capacity; and
- (d) increase the rate at which the hydrogen can be stored or retrieved from the alloy while maintaining good electrochemical parameters.

The well-studied LaNi<sub>5</sub>-based compounds can store reversibly about 1.35 weight percent hydrogen. Although this amounts to twice the density of liquid hydrogen, it is still too low for many terrestrial and aerospace applications. Researchers are investigating alloy materials with higher weight-percent hydrogen storage capacity, including alloys based on magnesium. Magnesium-based alloys can store about 5 weight percent hydrogen but the metal and the hydride are easily corroded in most electrolytes and thus have found no use as battery electrodes.

## Properties of Metal-Hydrogen (gas) Systems

Although the nickel/metal hydride battery operates in KOH electrolyte, much can be learned from studying the reaction of metals with hydrogen gas and such studies are always the starting step in the development of a new alloys for hydrogen storage. The equilibrium pressure-composition-temperature relationships of a metal/hydrogen system can be conveniently summarized by a P-C-T diagram of which an idealized version is showed in figure 2. The curve in the figure, called a P-C *isotherm*, gives the locus of equilibrium pressure-composition points for a given temperature. The P-C curve shows three distinct sections: Initially the isotherm ascends fast (section A-B) as hydrogen enters the metal lattice and occupies interstitial positions. By convention, this metal/hydrogen compounds is called the a-phase. At low concentrations of hydrogen, the composition/pressure relationship in the a-phase is ideal and obeys Sievert's Law, i.e.,

$$H/M = K_s P^{1/2} \quad (1)$$

where H/M is the hydrogen to metal ratio,  $K_s$  is Sievert's constant, and P is the equilibrium hydrogen pressure. As the hydrogen content in the metal increases, the hydrogen atoms interact (via the elastic strains introduced in the metal lattice) and the pressure/composition behavior departs from ideality. This is reflected by a decrease in the slope of the isotherm. However, there is a limit in the amount of hydrogen the a-phase can store. At a critical average hydrogen concentration, the metal/hydrogen system forms a new phase, the hydride phase, denoted as b. There is a discontinuity in the amount of hydrogen that the metal can store: at the temperature  $T_0$ , the maximum hydrogen solubility in the a-phase is  $c_1$  which is significantly lower than the minimum concentration  $c_2$  which can be stored in the b-phase. Typically,  $c_1 < 0.1$  whereas  $c_2 \approx 1$ . The flat, or *plateau* region in the P-C-T curve corresponds to the co-existence of the a and b phases.

As more hydrogen enters the metal, the volume fraction of the  $\alpha$ -phase decreases whereas that of  $\beta$ -phase increases. At the end of the plateau, all the metal/hydrogen alloy is  $\beta$ -phase. To force more hydrogen into the alloy requires increasing the external gas pressure. This is represented by the rapid increase in the C-D region of the P-C-T curve.

In general, the plateau pressure for hydrogen loading is different from that for unloading. This pressure difference is called *hysteresis* and although models have been proposed to explain the effect [ 5], further research is needed to fully understand it.

A flat plateau in the P-C curves is usually a required feature for gaseous hydrogen delivery systems (e.g., refrigeration suits for astronauts) because it means that a large quantity of hydrogen can be stored reversibly at a constant pressure. However, a flat plateau is not required when the metal hydride is used electrochemically because, according to Nernst equation applied to 6-molar KOH and near-ambient conditions of pressure and temperature, a change of one order of magnitude in the hydrogen gas pressure corresponds to an electrochemical potential change of only 29 mV. It is important, however, that the plateau be as wide as possible (large hydrogen storage capacity) and that at room temperature the plateau pressure be close to atmospheric pressure, since then the battery enclosure does not need to be especially strong.

## **Synthesis of Materials for Nickel/Metal hydride Batteries**

The physical and electrochemical characteristics of the alloys to be used as hydride electrodes are intimately related to their composition, metallurgy, and microstructure. Because of this dependence, the method for producing the alloys becomes an integral part in the optimization of their physico-chemical characteristics.

Arc melting in an inert atmosphere has been the traditional method for preparing  $\text{cm}^3$ -size alloys for research of hydrogen storage materials. This technique, though simple, fast, and economical, is of limited use when the alloy components have vastly different melting temperatures or high vapor pressures. Another shortcoming of arc melting is that while the molten alloy cools and solidifies, solute segregation may lead to partitioning into phases of different composition. Even when the alloy composition is within a single phase field, severe solute segregation may occur if, at that composition, the liquidus and solidus surfaces of the alloys do not osculate. In practice, alloys prepared by arc casting must be homogenized through a long high-temperature anneal.

Many of the shortcomings associated with arc melting are avoided when the alloy powders are prepared by mechanical alloying (MA). MA is a high energy ball-milling process that repeatedly cold welds and fractures powder particles. After a short milling period, the powder particles attain a layered morphology of the starting elements. The thickness of these layers decreases with increasing milling time and, after long attrition times, the powder forms a true alloy down to atomic dimensions. The alloy phases formed by MA are usually metastable, e.g., amorphous or nanocrystalline. These powders can be used in the as-prepared state or can be annealed to grow powder particles with large crystallites.

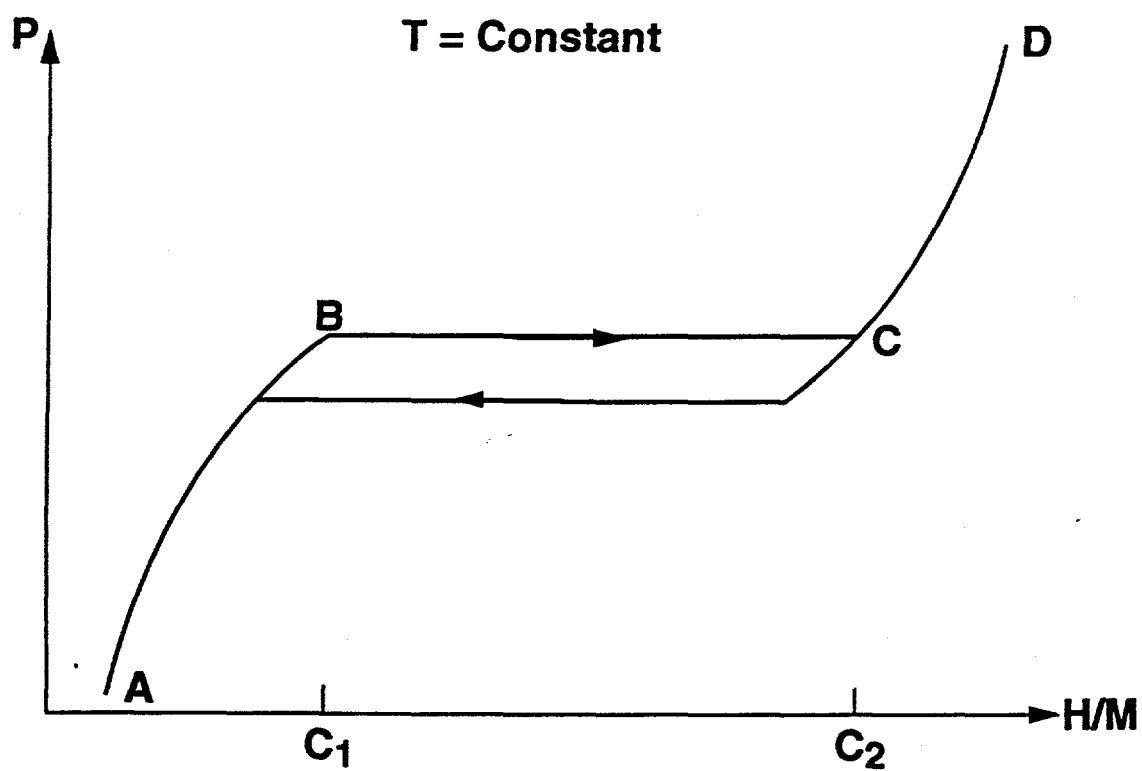
Amorphous metallic alloys have been investigated as potential hydrogen storage materials in both gaseous and electrolyte media. The main advantage of amorphous alloys is that they show little degradation in the hydrogen absorption/desorption capacity with cyclic loading. However, the metal/hydrogen equilibrium of amorphous and nanocrystalline alloys differs substantially from that of alloys having large crystallites (crystallite dimensions larger than about 1  $\mu\text{m}$ ). Whereas the P-C curves of crystalline materials usually have well-defined plateaus, the P-C curves of amorphous and nanocrystalline alloys have narrow or nonexistent plateaus. Amorphous alloys lack plateaus because the atomic sites at which the hydrogen atoms can reside are non-equivalent. Although the lack of a plateau may be a problem for the reversible storage of

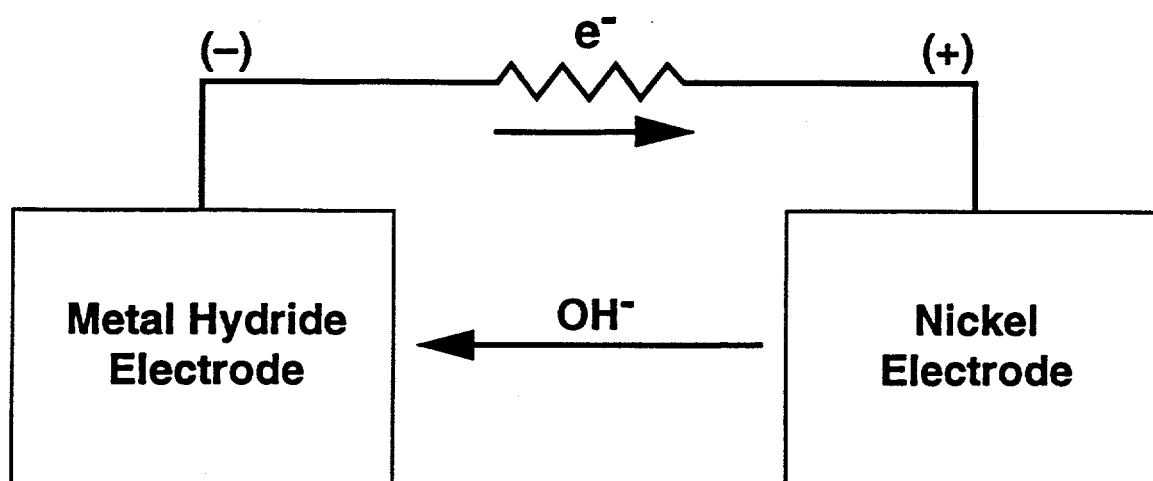


hydrogen gas, a 'sloping' plateau should not be a problem when the reversible charging is done electrochemically because, as mentioned earlier, a factor ten increase in the pressure is equivalent to a potential increase of only 30 mV. However, amorphous metallic alloys have so far found little application for reversible electrochemical hydrogen storage.

Other advantages of the MA synthesis route are described below:

- Σ Using MA it is easy to alloy elements which have vastly different melting temperatures. This is much more difficult to do with conventional casting techniques since on heating, the lower melting temperature components boil and tend to vaporize before reaching the melting temperature of all components.
- Σ With MA, powders can be prepared containing particles which have a layered microstructure of two or more elements or phases. This enables fabricating two-phase particles in which one of the phases is a catalytic material with the purpose of enhancing the kinetics of hydrogen absorption/desorption.
- Σ The powder particles prepared by MA have a unusual morphology which makes them less prone to comminution during cyclic hydrogen charging/discharging.
- Σ MA is a simple method for doping powder particles with a uniform distribution of nano-sized catalytic particles (e.g., Pt or Pd). Adding these particles is also possible using chemical techniques but MA permits a better distribution and mechanical contact between the catalysts and the particles.
- Σ MA can be used to prepare hydrogen storing powders such as  $\text{LaNi}_5$  starting from  $\text{La}_2\text{O}_3$  rather than from the more expensive metallic lanthanum. The starting material can also be a mishmetal oxide (a natural combination of rare earths). (DoE patent application being processed).
- Σ MA done under a low pressure of hydrogen can be used to prepare compounds such as  $\text{Mg}_6\text{Co}_2\text{H}_{11}$ , which cannot be prepared by simply forcing hydrogen into  $\text{Mg}_3\text{Co}$ , since this compound does not exist.
- Σ Nanocrystalline powders prepared by MA can be used as precursor phases for the synthesis of homogeneous alloys with grain sizes larger than 1 nm.
- Σ MA can be easily scaled up to industrial production of hydrogen storage powders using a proved and mature technology.





## HYDROGEN FUEL CELLS FOR UTILITY AND TRANSPORTATION APPLICATIONS

Shimshon Gottesfeld, LANL

To achieve high performance and high energy efficiency, hydrogen fuel cells depend critically on materials properties. For the intensively developed polymer electrolyte fuel cell, some key materials are:

- a) a polymeric membrane of high protonic conductivity and chemical stability
- b) a well designed thin film catalyst
- c) hardware materials required to maintain high bulk surface conductivity under demanding cell operating conditions

Polymer electrolyte fuel cells and their components will be discussed, highlighting key materials issues.

# The Polymer Electrolyte Fuel Cell: Materials Issues in a Hydrogen Fueled Power Source

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**Introduction:** Polymer electrolyte fuel cells (PEFCs) have attracted much interest recently. The need for an efficient, non-polluting power source for vehicles in urban environments, emphasized by recent legislative initiatives, has resulted in increased attention to the option of fuel-cell powered vehicles of high efficiency and low tail pipe emissions. Hydrogen is the most suitable fuel for a fuel cell powered vehicle, providing the highest conversion efficiency for fuel-on-board-to-electric-power and generating zero tail-pipe emission since water is the only product of the hydrogen/air fuel cell process. Hydrogen fuel could be carried on board the vehicle as either neat hydrogen, in the form of pressurized gas or cryogenically stored liquid, or in the form of a more ordinary liquid fuel, such as methanol or liquid hydrocarbon, which needs to be processed/converted on board the vehicle to a mixture of hydrogen and CO<sub>2</sub>. The latter type of vehicle will not satisfy the criteria of a "Zero-Emission-Vehicle" (ZEV), but may still satisfy the criteria for an Ultra Low Emission Vehicle" (ULEV).

Of various fuel cell systems considered, the polymer electrolyte fuel cell technology seems to be most suitable for terrestrial transportation applications. This is due to low temperature of operation (hence, fast cold start), perfect CO<sub>2</sub> tolerance by the electrolyte and a combination of high power density and high energy conversion efficiency. Key barriers for the development of this fuel cell technology for terrestrial applications, considered very high just 5-10 years ago, have been successfully overcome. As a result, automotive and fuel cell manufacturing industries have initiated significant technology validation programs and demonstrations which include fuel cell powered vehicles, stationary power generation systems and battery replacement devices. Market entry of PEFCs through the latter applications may actually precede implementation of such fuel cells in vehicular power systems, in large part because of less stringent demands on system's cost.

In this Mini-Workshop, we will show how novel materials and the R&D efforts towards their characterization and development, have advanced PEFC performance, lowered cost and enhanced reliability and, consequently, enabled the significant recent advancements in this fuel cell technology.

We specifically discuss the following subjects:

- (1) The Polymer Electrolyte Fuel Cell -- general description
- (2) Catalysts and the Membrane/Electrode Assembly
- (3) The Ionomeric Membrane

#### (4) Carbon and Metal Hardware Components for Gas Distribution and Current Collection

*The Polymer Electrolyte Fuel Cell: General Description:* We give first a general description of the polymer electrolyte fuel cell, highlighting central issues of materials requirements for this unique hydrogen fueled power source. In the text, we highlight *materials* to be discussed by using *italics*.

**Figure 1** is a schematic presentation of the cross-section of a single polymer electrolyte fuel cell (PEFC). This scheme will be used to discuss the key materials and processes in the PEFCs. The "heart" of the cell, which is magnified in the scheme, is the so-called *membrane-electrode (M&E) assembly*. In its simplest form, the "electrode" component of the M&E assembly would be a thin film (5-50  $\mu\text{m}$  thick) containing *dispersed Pt catalyst*. This catalyst layer is in good contact with an *ionomeric membrane*, the central slab in the scheme in figure 1, which serves as the electrolyte and the gas separator in the cell. The ionomeric membrane electrolyte is typically 50-175  $\mu\text{m}$  thick.

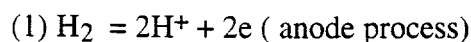
A M&E assembly thus consists of an ionomeric membrane with thin catalyst layers bonded onto each of its two major surfaces. It can be seen that the M&E assembly has the generic structure of an electrochemical cell: electrode/electrolyte/electrode, packaged in the form of a "sandwich" of three thin films. The "gas-diffuser" (or "backing") layers in immediate contact with the catalyzed membrane (see Fig. 1) are made of *hydrophobized porous carbon paper*, or carbon cloth. These layers are typically 100-300  $\mu\text{m}$  thick and are wet-proofed by treatment with *poly-tetrafluoroethylene* (PTFE). The role of these gas diffusers is to enable direct and uniform access of the reactant gases, hydrogen and oxygen, to the catalyst layers, without having to diffuse through films of liquid water.

The single cell is completed by current collector plates which usually contain machined flow fields, as required for effective distribution of reactant gases along the surfaces of the electrodes. These plates, traditionally made of *high density graphite*, become "bipolar plates" in the fuel cell stack, in which case they would have gas flow fields on both sides, as shown schematically in Figure 1. A general view of a single cell hardware is presented in Figure 2. The *Teflon* masks shown are gaskets that confine the gas flow to the active area and provide, together with the periphery of the ionomeric membrane, an effective seal. In a fuel cell stack, many such cells are stacked together to generate the voltage required for a given application, since a single hydrogen/oxygen fuel cell operated at only about 0.7V.

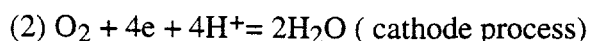
The above short discussion of the unit cell of a polymer electrolyte fuel cell stack, highlights different materials of unique characteristics (see italicized materials & components names), required to achieve a fuel cell power source of high performance, high energy conversion efficiency and stable long-term operation. We discuss them further below.

**Electrocatalysts:** Returning to the M&E assembly, the magnified part in Figure 1 highlights the central element of the PEFC which consists of a proton-conducting membrane electrolyte with a composite catalyst layer adjacent to each of its surfaces. The scheme shows the catalyst layer as Pt (small circles) supported on carbon (larger circles). This type of catalyst has been used in more recent developments of PEFCs. The *Pt/C* powder, prepared mostly by procedures based on colloid chemistry consists of Pt

particles about 2 nm in diameter, supported on carbon particles about 10 nm in diameter. *Pt is an essential catalyst* for the electrochemical conversion of hydrogen and oxygen at the anode and cathode of the fuel cell, respectively, into electric current ( electric power). In the hydrogen/air fuel cell, the processes at the anode and cathode, respectively, are:



and,



The *Pt/C* powder has to be intimately intermixed with recast ionomer to provide sufficient ionic conductivity within the catalyst layer. Thus, the catalyst layer can be described as a *Pt/C/ionomer composite*, where each of the three components are uniformly distributed within the volume of the layer. PEFC stacks fabricated at this point still use PTFE-bonded Pt black catalysts applied by hot-press to the ionomeric membrane. Such Pt-black- based catalyst layers typically require a Pt loading 20-40 times higher than that required in the *Pt/C* catalyst ( 4mgPt/cm<sup>2</sup> vs. 0.1 mg Pt/cm<sup>2</sup>) to obtain a similar cell performance. *Pt/C* catalysts will have to be adapted in commercial PEFCs because of their much lower cost and their intrinsic high performance and reliability. Work at LANL during the last five years has brought the low-Pt- loading M&E technology to the point of industrial realization, enabling an important lowering of the cost barrier to implementation of polymer electrolyte fuel cell technology.

***The Ionomeric Membrane:*** The *proton conducting polymeric membrane* is the most unique element of the polymer electrolyte fuel cell, as indeed reflected by any of the three names used for this type of cell: PEM fuel cell = Polymer Electrolyte Membrane fuel cell, SPE<sup>TM</sup> fuel cell = Solid Polymer Electrolyte Fuel Cell, or PEFC = Polymer Electrolyte Fuel Cell. The membrane commonly employed in most recent PEFC technology developments is made of a *perfluorocarbon sulfonic acid ionomer*.

*Nafion<sup>TM</sup>* made by DuPont is the most well known material of this type. Similar materials are produced as either commercial or developmental products by W.L. Gore ( US), Asahi Chemical and Asahi Glass ( Japan). The combined chemical and physical properties of perfluorocarbon sulfonate ( PFSA) membranes give them significant superiority over any other membrane material as electrolytic separators in PEFCs. These membranes exhibit very high long-term chemical stability under both oxidative and reductive environments, thanks to their Teflon-like molecular backbone. The protonic conductivities achieved in well humidified membranes are as high as 0.1 S/cm at cell operation temperatures, which translates to an "areal resistance" as low as 0.05 ohm cm<sup>2</sup> for a membrane 50 μm thick. Such a thin membrane can serve at the same time as an effective gas separator: the permeability of both oxygen and hydrogen through the membrane are both of the order of 10<sup>-11</sup> -10<sup>-10</sup> mol/cm-sec-atm, which translates to a gas cross-over equivalent current density of 1-10 mA/cm<sup>2</sup> through a 100 μm thick membrane in an operating fuel cell. This leakage current is at or below 1% of the operating current of a PEFC -- typically 1A/cm<sup>2</sup> or higher.

The two important drawbacks of PFSA membranes are the limited range of temperatures in which they can be effectively employed and their high cost at present. The first limitation typically forces operation of PEFCs at temperatures below 100°C,

although some increase of the temperature of operation, e.g., to 120°C, may be possible at the expense of operation under pressurized steam. The upper limit on the temperature is dictated by the need for effective humidification of the membrane, to maximize the protonic conductivity. This need also dictates, in turn, operation in a temperature/pressure domain corresponding to a dual phase (liquid-vapor) water system, which results in liquid water removal and/or liquid water recirculation requirements. The cost of the membrane is an issue outside the scope of our discussion. However, it can be predicted with reasonable certainty that this cost may come down significantly as the market for the membrane will significantly increase, e.g., as a result of large scale application in electric vehicles.

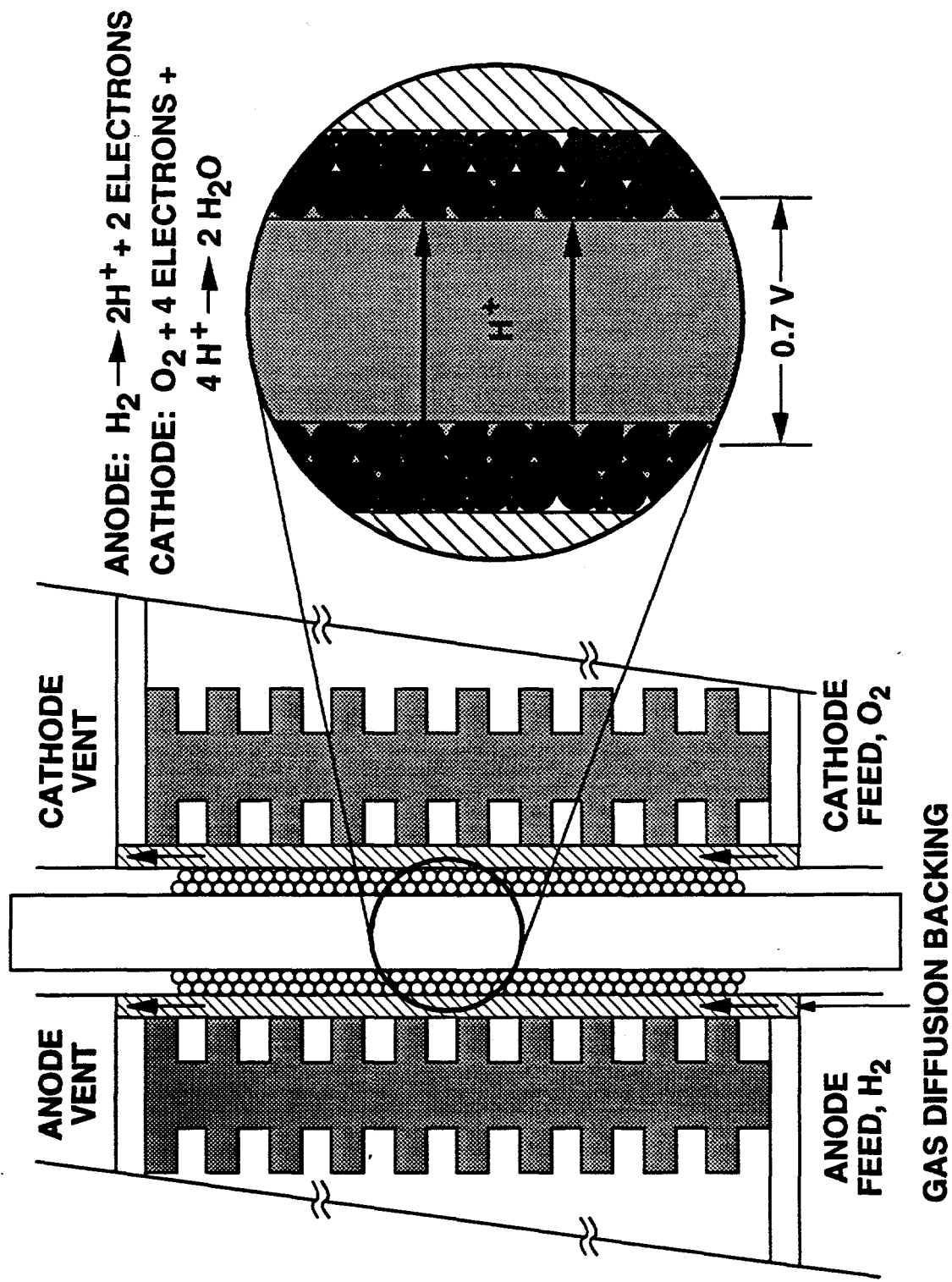
**The Gas Diffuser:** The porous backing layer which is placed behind the catalyst layer (Figure 1) fulfills important tasks in the PEFC. In this layer, combined requirements of effective reactant gas supply to the catalyst layer and effective water supply and removal in either vapor or liquid form have to be simultaneously fulfilled. Wet-proofing by PTFE is required to ensure that at least part of the pore volume in the cathode backing remains free of liquid water in an operating cell, so as to enable rapid gas-phase transport. The scale of the porosity and the amount of PTFE added are two important parameters that determine the success of the backing layer in fulfilling the combined tasks of gas and water transport. Obviously, the backing layer has to be made of a material of high and stable electronic conductivity in a wet environment. Although some expanded metal structures have been suggested, most of PEFC backings to date have been based on porous carbon paper or cloth.

**Graphite vs. Metal Hardware for Gas Distribution/Current Collection:** The final element on the outer side of the unit cell (Figures 1 and 2) is the current collector plate which typically contains a machined gas flow field. These two functions of current collector and gas flow field may be fulfilled, in principle, by two separate components but, in most of the cells and stacks tested to date the flow field is machined in the current collector plate using a range of geometries, e.g., a single serpentine channel, parallel channel flow and series-parallel combinations. The flow-field geometry may be quite significant in fulfilling the requirements of effective water supply and effective liquid water removal from the cathode. The current collector plate becomes the bipolar plate in a PEFC stack. It should therefore exhibit high electronic conductivity and be impermeable to oxygen and hydrogen gas. Both carbon and metals like stainless steel or titanium have been considered as potential materials for the current collector, or bipolar plate as it would be called in the context of a stack.

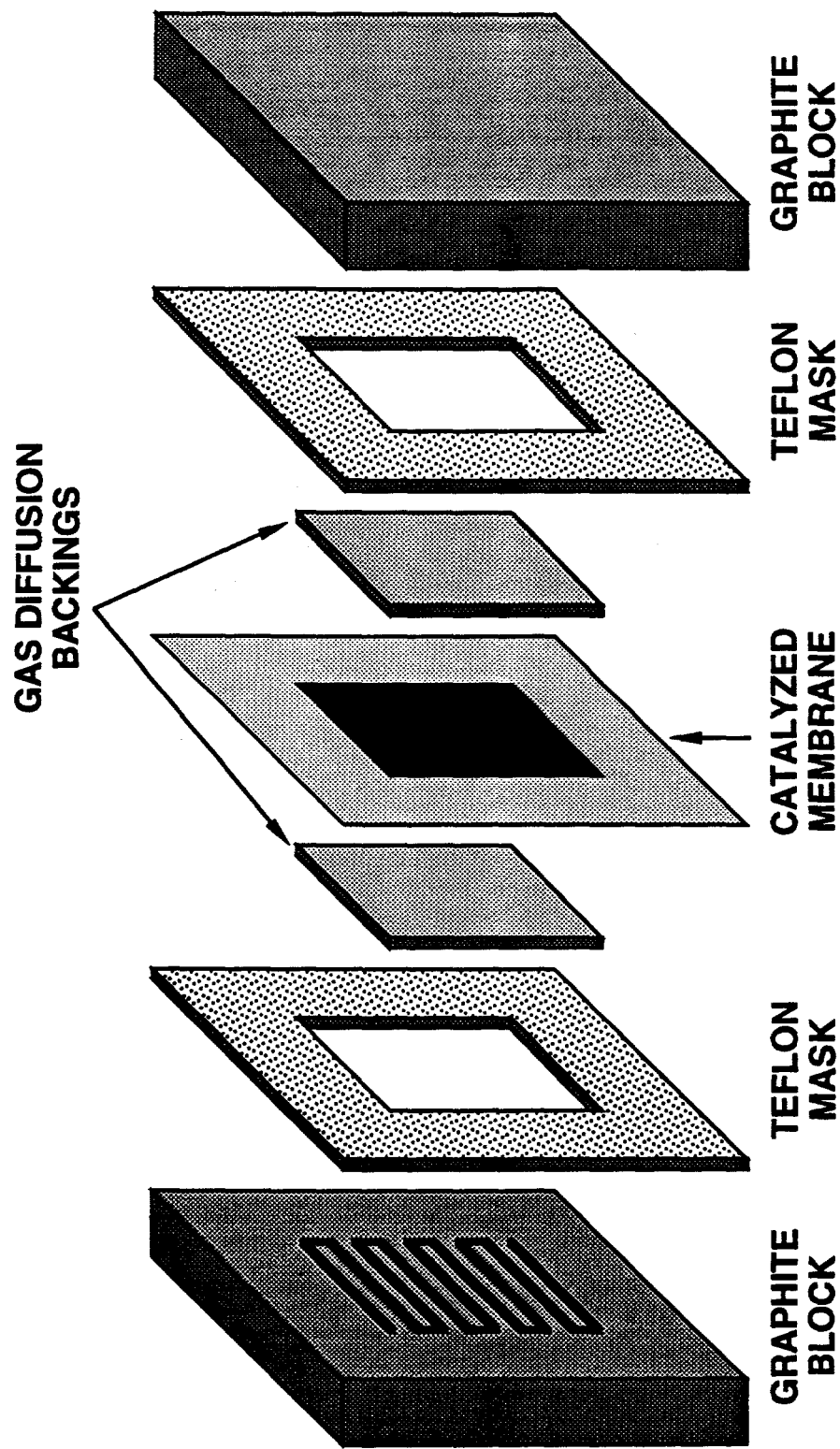
The very general description provided above for the component parts of a PEFC should clarify the diversity of R&D elements involved in the development of a PEFC cell and stack. These R&D elements span fields of research in interfacial electrochemistry (electrocatalysis), electrochemistry and materials science aspects of membranes, carbon and metals, and mass/heat transport engineering. This Workshop covers some highlights of LANL work on electrochemical and materials aspects of the PEFC as well as the building and testing of cells based on improved materials and electrocatalysts. In most general terms, the target of these efforts in development of materials and components has been to achieve high PEFC performance, long-term performance stability and low intrinsic cost.



# CROSS SECTION OF POLYMER ELECTROLYTE FUEL CELL



# SINGLE CELL HARDWARE



## MINI-WORKSHOP:

### ENGINEERING MATERIALS FOR HYDROGEN SEPARATION

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The use of hydrogen gas has become more important in recent years to a variety of high technology areas, such as microelectronics, ferrous and nonferrous metals processing, chemical and polymer synthesis, and petrochemical processing. Further, the steady depletion of limited-resource fossil fuels, such as light crudes and natural gas, and the associated pollution problems have made hydrogen-based energy systems more attractive. As such, the production of pure hydrogen gas for use in these areas has become more important.

In this workshop, the purification of hydrogen gas from impure feed streams using high temperature membranes will be examined. The fundamental differences in the way that hydrogen interacts with metals will be demonstrated. From these differences, we will be able to explain how one can design and engineer a membrane to exploit the advantageous properties of multiple materials into a composite structure with superior performance. One will gain hands-on experience with flow rate determination, gas analysis with mass spectrometry, and observe structural changes in metals due to hydrogen by x-ray diffraction.

# ENGINEERING MATERIALS FOR HYDROGEN SEPARATION

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**Key Words:** Hydrogen separation, x-ray diffraction, mass spectroscopy.

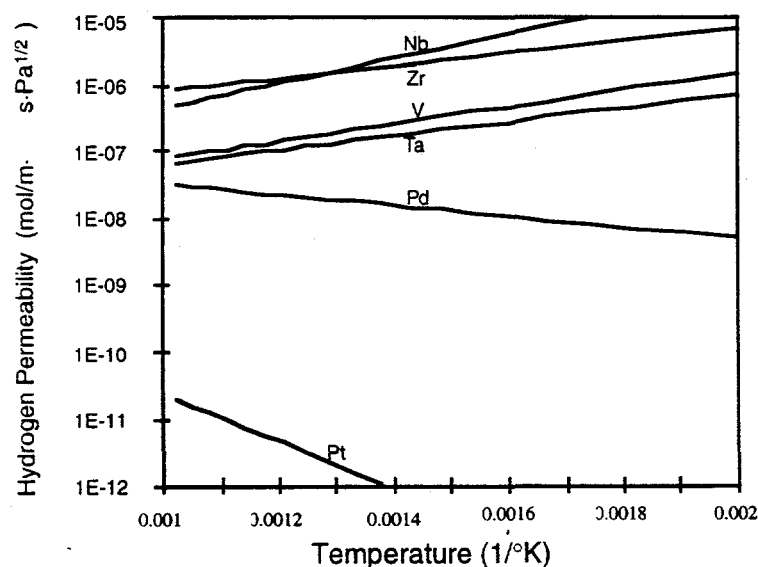
**Prerequisite Knowledge:** Because hydrogen gas is used in this workshop, a working knowledge of *hydrogen safety is required*. Basic Materials Science is helpful but not necessary.

**Objective:** To understand the fundamentals of designing and engineering membranes for the purpose of hydrogen separation and to learn about the characterization and testing equipment that is used in experimental evaluation of these materials.

## Introduction:

With the steady depletion of fossil fuel reserves, hydrogen based energy sources are becoming increasingly more attractive. This drive is creating a continued and building interest in developing economically viable methods for hydrogen production and separation from alternative hydrocarbon sources, such as natural gas and methanol. Although hydrogen selective membranes have been considered and applied in this area, their use has been minimal because of their high cost and limited lifetime due to embrittlement. The most popular metal used for hydrogen separation has been palladium and its alloys; these materials and their interaction with hydrogen have been well studied, with published work dating back over one hundred years.<sup>1</sup> While palladium is an attractive membrane material because of its ability to readily dissociate molecular hydrogen into atomic hydrogen, several inherent problems remain.

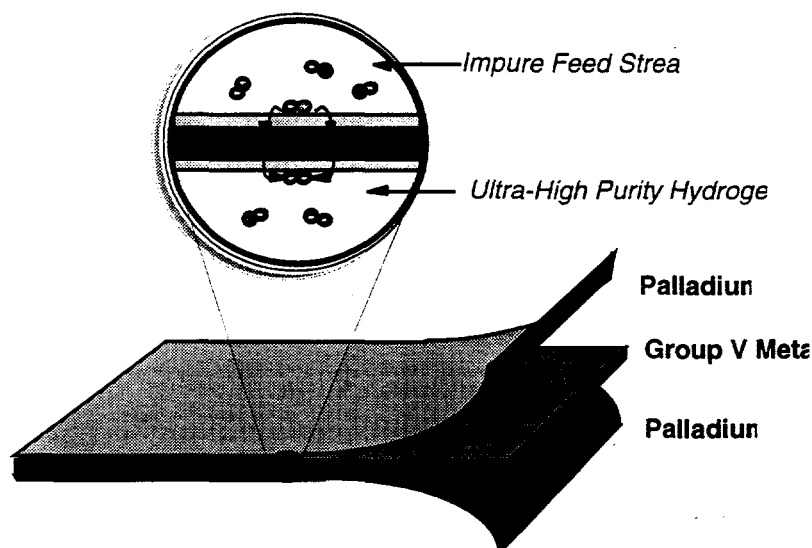
First, palladium undergoes an  $\alpha$ - $\beta$  phase transformation at temperatures below 300°C; the actual transformation temperature depends on the hydrogen concentration in the metal.<sup>2</sup> Expansion and contraction of the lattice from the phase transformation leads to embrittlement and fracture of the metal. Some control of this problem can be gained by alloying the palladium with silver. Inclusion of silver significantly reduces the critical temperature and pressure of the phase transformation.<sup>3</sup> This reduces the embrittlement



**Figure 1. The bcc-refractory metals have a higher transport rate than palladium.**

of the metal and extends the lifetime of the membrane. However, these alloys are still very expensive because the bulk of the material is still dominated by the palladium cost.

Furthermore, the bulk transport of hydrogen in face centered cubic (*fcc*) metals, such as palladium and palladium alloys, is inherently lower than in a number of refractory, body centered cubic (*bcc*) metals.<sup>4-5</sup> As seen in Figure 1, zirconium, niobium, tantalum, and vanadium all have significantly higher bulk hydrogen permeabilities than does palladium.<sup>6</sup> Unfortunately, the direct replacement of palladium for cheaper refractory metals as membranes is not possible because of the lack of catalytic ability and because of the self-passivating oxide layers formed on these metals which slow the flux of hydrogen through the metals.



**Figure 2.** The composite membrane has thin palladium layers on both sides of a Group V-B metal foil.

To exploit the rapid bulk diffusion of hydrogen through the refractory metals, a composite structure can be fabricated where a thin palladium layer is placed on each side of the *bcc* metal. This allows the dissociation of the molecular hydrogen by the surface palladium layer, transport through the refractory metal bulk, and finally reassociation on the opposite palladium surface. This composite membrane is shown in Figure 2. Such a structure has several advantages.

First, greater overall hydrogen fluxes are possible because bulk diffusion is not limited by the *fcc* structure of the palladium. The membrane structure can then be thicker providing improved mechanical stability while still yielding acceptable gas fluxes. Second, because these refractory metals are significantly cheaper than palladium and only two thin layers ( $< 5,000\text{\AA}$ ) of palladium are required, these membranes are much more economical. While the Group V-B metals are still subject to hydrogen embrittlement, the temperature where this is a problem is well below room temperature.<sup>7-8</sup> Finally, should the surface palladium layer develop a crack or multiple defects, the membrane would not catastrophically fail. Instead, only a minuscule portion of the membrane would be made inoperative.

The obvious advantages of this composite metal membrane have not escaped previous investigators. Indeed, about 30 years ago, Makrides filed a patent for plating foils of Group V-B metals with thin layers of palladium.<sup>9</sup> In recent years, additional patents have been filed by other groups for similar structures.<sup>10-12</sup> While it is clear that viable composite membranes have been constructed, improvements of the material are still required to make these structures more efficient. A critical area for improvement is the removal of the surface oxide layer which forms as a self passivating layer when the pure metal is exposed to the atmosphere. Various chemical and mechanical techniques have been used to achieve a stripping of this layer but most allow some amount of regrowth of the oxide before coating with the palladium layers. Another area of concern is the quality of the palladium layers.

To address the need for enhanced hydrogen separation techniques using metal membranes, a different fabrication technique was utilized that would overcome these

concerns. The objectives for the fabrication were: obtaining a highly clean surface on the refractory foil, forming a palladium coating without subsequent surface contamination, and providing a high degree of purity, crystallinity, and crystallographic orientation. To achieve these objectives, the process of physical vapor deposition was used. Within a high vacuum chamber, both sides of a tantalum or vanadium foil were ion milled to remove the surface oxide and, without ever breaking the vacuum, both sides of the cleaned foil were coated with thin palladium layers. The palladium was deposited using either e-beam evaporation or sputtering. Foils produced by this technique have yielded exceptionally high hydrogen flow rates.<sup>13</sup>

### Membrane Characterization:

After the membranes have been fabricated in the deposition system, they need to be characterized to determine the crystalline phases that are present and the crystallographic orientation of these phases. By determining a picture of the membrane composition before passing hydrogen through, the effects of the hydrogen transport can be better determined and the effect of the deposition parameters can be correlated to the observed permeability of the membrane. Among the available characterization techniques, the process of x-ray diffraction (XRD) has proved to be the most effective.

XRD is a non-invasive technique, i.e., the membrane does not have to be destroyed to undergo the testing and is typically not affected by the characterization process. The most common and versatile diffractometer geometry is the theta-2 theta. In this type of diffractometer, x-rays are generated from a metal target, typically made of copper; these x-rays are focused onto the sample which is fixed at an angle of theta degrees to the beam. A detector collects the reflected x-rays from the sample and is held at an angle of 2 theta to the sample. The sample and the detector are moved through a range of theta-2 theta angles, and data is constantly collected for analysis, typically using a computer interface. Peaks in the reflected x-ray signal, as recorded by the detector, correspond to the presence of particular crystalline phases. The diffraction peaks are related to the characteristic d-spacing of the material using Bragg's Law:

$$n\lambda = 2d \cdot \sin(\theta)$$

where n is any integer and is usually taken as 1,  $\lambda$  is the wavelength of the x-rays used in Å, d is the characteristic d-spacing of the crystalline phase in Å, and  $\theta$  is the angular position of the peak. This data can later be used for a number of purposes, such as qualitative and quantitative phase analysis, particle size measurements, particle micro- and macro-strain estimation, and texture/preferred orientation determination. For a better and more complete explanation of the process of x-ray diffraction, a number of sources are available.<sup>14-15</sup>

For the purposes of characterizing the membrane, the most important features of the diffraction trace is the identification of all of the peaks and the relative intensities of the peaks. By identifying the peaks, it is possible to determine if the membrane contains any impurities, such as oxides or hydrides, left over from the deposition process or the exposure to hydrogen. This is done by matching the peak locations, usually determined by the computer software, to a set of published values, such as those found in the JCPDS powder diffraction files. After all of the peaks have been attributed to the known phases, i.e., palladium and vanadium/tantalum, any remaining peaks must be identified to the contributing phase. Also of importance are the relative peak intensities, supplied by the computer software. By comparing the intensities before and after the exposure to hydrogen, it is possible to learn about the effect of hydrogen transport on orientation of the grains, especially along particular crystallographic directions. Of interest are the close packed planes in the metals: the 111 planes for the bcc structure and the 110 planes for the fcc structure.

### Membrane Testing:

The ability to properly and effectively test the performance of the membrane is important and requires a carefully designed testing apparatus. A schematic of the one developed and used at Los Alamos National Laboratory is shown in Figure 3. This system allows for the testing of membrane efficiency and hydrogen purity and flow rate as a function of several variables, such as temperature, feed and permeate pressures, feed composition, and total flow rate. The membrane test system consists of a membrane holder unit in which the membrane is sealed between the feed and permeate streams. Up to four constituents can be used in the feed supply and feed flows are controlled using independent MKS mass flow controllers so that mixtures of various compositions can be used. The pressure on the feed side of the membrane is controlled by either pumping using a turbo pump (in the case of sub-atmospheric pressures) or by restricting the flow of the exhaust from the feed side using a needle valve (in the case of elevated pressures). The pressure of the feed is measured using a Baritron pressure transducer for pressures up to 1000 torr and using a dial gauge for higher pressures. The permeate side of the membrane allows the gas flow to pass through an MKS mass flow meter to determine the flow rate of gas passing through the membrane. The pressure on the permeate side of the membrane is also controlled either by pumping for low pressures or by restricting the flow for high pressures. The composition of both the feed and permeate gas streams can be analyzed using a Residual Gas Analyzer (RGA).

The testing system contains an RGA which uses a quadrupole mass spectrometer to determine the particular species and isotopes and their relative amounts present in the gas stream. The quadrupole mass spectrometer consists of four cylindrical rods to which a combination of a.c. and d.c. potentials are applied. For a given applied a.c. frequency, only

ions of a particular value of  $e/m$  can pass through to the collector. The spectrum of  $e/m$  ions is collected by varying the a.c. frequency through a programmed range or through selected values. The mass spectrometer is important in the testing of the membrane because it can determine the purity of the gases that are passing through the membrane. This information can then be used to determine if the membrane is not completely selective to hydrogen only or if it has developed a leak. Furthermore, the relative passage rate of various isotopes can be determined from the spectrum.

### Conclusions:

In this paper, the method by which a novel metal membrane for the separation of ultra high purity hydrogen gas from an impure feed stream has been described. This composite metal membrane having exceptionally high hydrogen flows was fabricated using palladium coated Group V-B foils. The cleaning of the refractory metal using ion milling and subsequent deposition of the palladium layer in the same vacuum chamber provides a method of constructing a membrane having high purity, crystalline palladium bonded to a very clean metal foil surface. The characterization and testing apparatus has also been

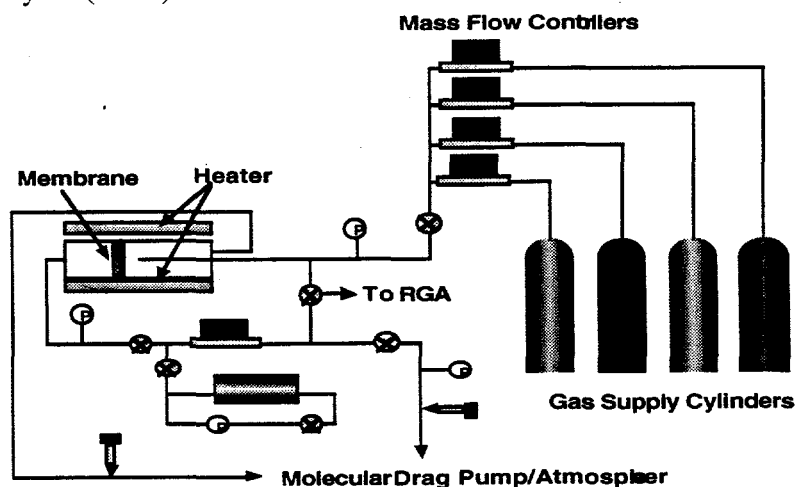


Figure 3. Permeation testing apparatus.

described, with particular attention paid to the processes of x-ray diffraction and mass spectrometry. These two techniques provide the most versatile and revealing insight to the structure and performance of the membrane. By using several different techniques, an integrated solution has been engineered to a problem to produce a material that has superior performance to anything that has come before.

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12. D.J. Edlund, Composite Hydrogen Separation Metal Membrane, US Patent 5,393,325, Feb. 28, 1995.
13. N.M. Peachey, R.C. Snow, R.C. Dye, and S. Birdsell, Composite Metal Membranes for Hydrogen Separation, US Patent applied for.
14. B.D. Cullity, Elements of X-Ray Diffraction, 2nd Ed., Addison-Wesley, Reading, MA (1978).
15. H.P. Klug and L.E. Alexander, X-Ray Diffraction Procedures, 2nd Ed., Wiley, New York (1974).



# A CURRICULUM OUTLINE FOR TEACHERS

## MAKE YOUR OWN ENERGY

### FUNDAMENTAL ISSUE: ACHIEVING EFFICIENT, SECURE, AND ENVIRONMENTALLY SUSTAINABLE ENERGY SYSTEMS

#### PROBLEM:

There is a finite source of fossil fuels  
There is a need to develop demonstrations and pathways for sustainable energy systems

#### INDUSTRIES AFFECTED:

Transportation  
Utility  
Fuel merchants  
Chemical markets

#### ISSUES:

New areas of R&D  
New infrastructures  
New safety procedures

#### ACTION:

Education  
Demonstrations  
Pathways

### Fundamental Issue: Why is Hydrogen an Appropriate Alternative Fuel

#### • History

Cavendish/Lavoisier  
balloons  
Jules Verne  
J.B.S. Haldane  
20th century -- Francis Bacon/Daimler Benz/NASA/town gas

#### • Public perception

Hydrogen bomb  
Hindenburg  
The Challenger

#### • Fundamental chemical and physical properties

Lightest  
Most abundant (93 percent of all atoms)  
Exists in combination with other elements  
Low energy density  
Secondary form of energy  
Primary energy sources  
Natural gas  
Coal

- Biomass
  - Renewable sources
- Hydrogen production
  - Fossil fuel sources
    - Natural gas
    - Coal
  - Electrolysis
  - Renewable sources
    - Solar
    - Wind
    - Biomass
    - Hydro-power
    - Photobiological/photochemical
    - Electrolysis
- Cost of production
- Hydrogen storage
  - Pressurized gas
  - Liquid
    - Cryogenics
  - Metal hydride
  - Hydrogen and iron oxide
  - Glass microspheres
  - Adsorption
  - Fullerenes
- Utilization
  - Transportation
    - Internal combustion engine
    - Fuel cell
  - Utility/power generation
  - Battery replacement
- Distribution and infrastructure
  - Pipeline
  - Road and rail vehicles
  - Marine tanker
- Safety
  - Wide flammability range
  - High diffusivity
  - Buoyant
  - Odorless/colorless
  - Low ignition energy
  - Non-toxic
  - Materials embrittlement
  - Leak rate
- Short Term Applications of Hydrogen
  - Chemical feedstock/fertilizers
  - Gasoline refining
  - NASA/space technology
- Long Term Applications of Hydrogen
  - Energy storage
  - Energy carrier
    - Transportation fuel
    - Aircraft fuel
    - Utility fuel for heat and electricity

- Industries involved
  - Merchant hydrogen manufacturers
  - Utility companies
  - Fertilizers
  - Oil/gas
  - Fuel cell manufacturers
  - Aerospace
  - Automobile manufacturers
  - Consumer electronics

## **ENERGY CONVERSION**

- Energy has different forms: chemical (fuel), thermal, electrical
- How to convert one form of energy to another
- Less Efficient Multi-conversion processes:
  - Conventional Power Plant: Chemical to thermal to electrical
  - Car with IC Engine: Chemical to thermal to mechanical
- More Efficient conversion process:
  - Chemical to electrical directly: FUEL CELL
- Electrochemical cells
  - Device enabling direct conversion from chemical to electrical energy
    - Examples: Batteries, fuel cells
    - Commonalities and Differences between the two:
      - Common: Both convert directly chemical energy to electrical energy
      - Difference: In battery, the chemicals required for battery process are limited in amount and stored within battery
      - In fuel cell, the chemical reactants are unique in nature (fuel and oxidant -- oxygen or air) and stored outside cell in containers.

## **WHAT IS A FUEL CELL**

- History
  - Grove
  - Bacon
  - NASA
- Current technology
  - Electrodes and electrolytes
  - Membranes
  - Types of fuels -- highlighting hydrogen as cleanest and as enabling highest fuel cell efficiencies
  - System integration
- Energy conversion efficiencies
- Short term applications
  - Utility power generation
  - Demonstration/fleet vehicles
  - Demonstration of small scale replacement for batteries for consumer applications
- Long term applications
  - Transportation
    - Passenger vehicles
    - Locomotives
    - Boats

- Battery and generator replacement
- R&D issues
- Industries involved
  - Fuel cell manufacturers
  - Automobile manufacturers
  - Utility industry
  - Fuel suppliers

### **SOLAR HYDROGEN ENERGY ECONOMY**

- Electricity and hydrogen
  - Issues of interchangeability and singularity
  - Storage
  - Ability to transport energy
  - Cost
  - System efficiency
- Transitional system
  - Rapid implementation in demonstrations
  - Long-term commitment
  - Early high cost
- Energy Policies
  - Current (real) cost of fuels
  - Externalities
  - Life cycle analysis/buying habits

### **HOW DO YOU MAKE YOUR OWN ENERGY?**

#### **CLASSROOM ACTIVITY**

- Build energy system
  - Solar energy in ---> hydrogen out---> fuel cell application
- Technologies
  - PV or appropriate solar technology
  - Electrolyzer
  - Hydrogen storage
  - Fuel Cell
- Some related issues
  - Efficiency
    - Resource cycles (coal to electricity/ pv to electricity, etc.)
  - Energy audit, etc.

### **ENVIRONMENTAL IMPACTS**

- Full cycle energy use analysis
- Internal combustion vehicle vs fuel cell vehicles
- Greenhouse gases
- Carbon dioxide

# RESOURCES

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# INTERNET CONNECTIONS

## EDUCATIONAL LINKS

**American Hydrogen Association**

<http://www.getnet.com:80/charity/aha/>

**Center for Renewable Energy and Sustainable Technology**

<http://solstice.crest.org/index.html>

**Energy Directory -- Hydrogen and Fuel Cells**

<http://www.energy.ca.gov/energy/earthtext/other-hydrogen.html>

**EnviroLink Network**

<http://www.envirrolink.org>

**Gridwise Power Guide**

<http://www.gridwise.com/>

**The Hydrogen Research Institute**

[http://www\\_hydrogene.UQTR.UQuebec.ca/hydrogene\\_ang.html](http://www_hydrogene.UQTR.UQuebec.ca/hydrogene_ang.html)

**The National Hydrogen Association**

<http://www.ttcopr.com:80/nha/>

**North American Association for Environmental Education**

<http://nceet.snre.umich.edu/naaee.html>

**Why Use Hydrogen?** <http://www.humnat.org/hydro.html>

## GOVERNMENT LINKS

**Argonne National Laboratory** <http://www.anl.gov/OPA/overview.html>

**Hydrogen InfoNet** <http://www.eren.doe.gov/hydrogen/infonet.html>

**Morgantown Energy Technology Center**

[http://www.metc.doe.gov/research/power/fc\\_proje.html](http://www.metc.doe.gov/research/power/fc_proje.html)

**National Renewable Energy Laboratory** <http://www.nrel.gov>

**Oak Ridge National Laboratory** <http://www.ornl.gov>

**The President's Council on Sustainable Development** [http://www.whitehouse.gov/WH/EOP/pcsd/#general\\_information](http://www.whitehouse.gov/WH/EOP/pcsd/#general_information)

**South Coast Air Quality Management District** <http://www.aqmd.gov>

**U.S. Department of Energy, Hybrid Electric Vehicle Program - Hydrogen**  
<http://www.hev.doe.gov:80/components/hydrogen.html>

**U.S. Department of Energy, Energy Efficiency/Renewable Energy Network**  
<http://www.eren.doe.gov>

## **INTERNATIONAL LINKS**

**The NECAR from Daimler Benz** [http://daimlerbenz.com/spotlite/necar/necar\\_e.htm](http://daimlerbenz.com/spotlite/necar/necar_e.htm)

**The WE-NET Project (World Energy Network)**  
<http://rpgopher.aist.go.jp:8000/nss/text/WENET.html>

**The New Sunshine Program** [http://www.aist.go.jp/nss/text\\_HP.html](http://www.aist.go.jp/nss/text_HP.html)

**United Nations Environmental Program Collaborating Centre on Energy and Environment** <http://www.risoe.dk/sys/syshomeb.html>

**Energy Information on Internet from the Netherlands Energy Research Foundation**  
<http://www.risoe.dk/sys/syshom3b.html>

**Energy and Environment Sites from The World Bank**  
[http://www.worldbanl.org/html/fpd/em/em\\_net/insites.htm](http://www.worldbanl.org/html/fpd/em/em_net/insites.htm)

**EnviroNET Australia** <http://www.erin.gov.au/net/environet.html>

## **FUEL CELL DEVELOPERS**

**AlliedSignal** <http://www.alliedsignal.com>

**Ballard Power Systems, Inc.** <http://www.ttcorp.com/nha/ad12daim.htm>

**DAIS Corporation:21St Century, Fuel Cell Technology Division** <http://dias.net>

**ElectroChem, Inc.** [http://www1.usa1.com/~fuelcell/electrochem/PEM\\_Power\\_Unit.html](http://www1.usa1.com/~fuelcell/electrochem/PEM_Power_Unit.html)

**Energy Partners, Inc.** [http://www.gate.net/~h2\\_ep](http://www.gate.net/~h2_ep)

**Energy Research Corp.** <http://www.ercc.com>

**H Power, Inc.** <http://home.earthlink.net/~hpower/>

**ONSI Corporation** <http://www.utilicorp.com/Partners/ONSI.htm>

## **OTHER FUEL CELL RELATED SITES**

**Electric Power Research Institute** <http://www.epri.com>

**Gas Research Institute** <http://www.gri.org>



**Hydrogen & Fuel Cell Newsletter** <http://solstice.crest.org/renewables/thl/index.html>

**Sacramento Municipal Utility District** <http://www.smud.org/>

**Westinghouse** [http://www.metc.doe.gov/projfact/power/fc/west\\_so.html](http://www.metc.doe.gov/projfact/power/fc/west_so.html)

## **INTERNET NEWSGROUP**

[news.sci.energy.hydrogen](mailto:news.sci.energy.hydrogen)

## **JOURNALS FREQUENTLY CONTAINING RELEVANT ARTICLES**

ELECTROCHIMICA ACTA

ENERGY POLICY

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY

JOURNAL OF CHEMICAL EDUCATION

JOURNAL OF ENERGY RESOURCE TECHNOLOGY

JOURNAL OF THE ELECTROCHEMICAL SOCIETY

JOURNAL OF MATERIALS EDUCATION

JOURNAL OF POWER SOURCES

MATERIAL SCIENCE FORUM

PLATINIUM METAL REVIEW

SOLID STATE IONICS

## **USEFUL PHONE NUMBERS**

Department of Energy Bulletin Board (202)586-2557

National Alternative Fuels Hotline 1-800-423-1DOE

Energy Efficiency/Renewable Energy Clearinghouse 1-800-DOE-EREC

## **HYDROGEN: AN ENERGY CARRIER OF THE FUTURE**

Hydrogen is an energy carrier with the potential to join electricity as a key component of a sustainable energy system. As an energy carrier and fuel, its future integration into the energy economy will help make renewable energy sources viable and practical.

In the United States, the primary source of energy is the burning of fossil fuels—coal, natural gas, and petroleum. Uranium, used in nuclear power plants to generate electricity, is also a primary source of energy. Increasingly, renewable and sustainable sources of energy—sunlight, wind power, biomass, geothermal resources, and hydroelectric power—are contributing to meeting our nation's primary energy needs.

Primary sources are used directly to provide energy for services, but often they are used to create an energy carrier, such as electricity, to move the energy from the place of production to where it is needed to provide goods and services for society. Hydrogen has the potential to be a more versatile energy carrier than electricity. In the future, it may be produced cost effectively from renewable energy sources, then stored and transported for use in home and office heating, generating electricity, industrial processes, and surface and air transportation. It can accomplish this while also preventing pollution by substituting for and reducing the use of fossil fuels.

The benefits of hydrogen make it the ideal component of a renewable, sustainable energy system of the future. It can be produced from water—an abundant supply source—using direct sunlight, renewable electricity, and some biological organisms. When burned directly as a fuel, or converted to electricity, its primary emission is water, which can be safely returned to the environment or reused to produce more hydrogen.

The versatility of hydrogen will enable the more rapid expansion of the use of domestic renewable energy sources than might occur with electricity alone, resulting in reduced energy imports. Hydrogen energy has the potential for substantially contributing to the reduction of climate- changing emissions and other atmospheric pollutants.

Unfortunately, the widespread use of hydrogen energy is not currently feasible because of economic and technological barriers. Hydrogen is presently used in a variety of industrial applications and, from this base, research and development will move hydrogen into widespread energy applications.

### ***CURRENT UTILIZATION IN INDUSTRY***

Hydrogen is produced on an industrial scale from natural gas by steam reforming. In this process, thermal energy is used to separate hydrogen from the carbon component of natural gas (see box). Hydrogen is also produced as a by-product of petroleum refining and chemical production processes. Limited quantities of hydrogen are currently produced from the electrolysis of water (see box). This is presently a very expensive process, and is restricted to meeting the limited need for extremely pure hydrogen for manufacturing and the space program.

Current production prices for hydrogen gas produced by steam reforming range from \$7.00 per gigajoule for a large plant to \$12.00 per gigajoule for a small-capacity plant, assuming a natural gas price of \$2.30 per gigajoule. Production by electrolysis using low-cost, off-peak hydroelectricity costs between \$10.00 and \$20.00 per gigajoule. The current cost of electrolytic production using electricity from renewable energy sources is about \$28 per gigajoule. This cost is expected to be reduced to about \$8 per gigajoule by 2030 with continued strong research and development.

#### **Hydrogen Production from Steam Reforming**

Steam reforming is a method of deriving hydrogen from hydrocarbon fuels, such as natural gas, methane, and ethanol. The process involves the reaction of gaseous methanol and steam on catalytic surfaces. The first part of the reaction consists of methanol decomposing to hydrogen and carbon monoxide. The second part is called "shift reaction," and consists of carbon monoxide and water changing to carbon dioxide and hydrogen. The reactions occur at temperatures of 200°C (392°F) or greater and require heat to be input to the process.

Annual U.S. production of hydrogen for 1993 was about 5 billion cubic meters (178 billion cubic feet). Major uses are ammonia production and the removal of sulfur from petroleum during the refining process. Hydrogen for most large-scale applications—levels greater than 1.5 million cubic meters per day (50 million standard cubic feet per day)—is produced at the site where

it will be used. Hydrogen is used in smaller quantities in chemical processing, food hydrogenation, steel- and glass-making, and electronics. For these applications, hydrogen is delivered by truck as a compressed gas or liquid.

## ***HYDROGEN UTILIZATION IN ENERGY***

At present, hydrogen's only significant use as a fuel is in the U.S. National Aeronautics and Space Administration's (NASA's) space program. Liquid hydrogen and liquid oxygen are combined as propulsion fuel for the space shuttle and other rockets. Onboard fuel cells using hydrogen and oxygen also provide most of the shuttle's electric power. The fuel cell's only exhaust is pure water, which is used by the crew as drinking water (see box for a discussion of fuel cells).

Because of its versatility and many benefits, it is anticipated that hydrogen will be used in ever-increasing quantities in energy applications. Hydrogen exhibits clean combustion with no carbon or sulfur oxide emissions and very low nitrogen oxide emissions, and is capable of conversion directly to electricity in fuel cells with no pollution.

### **Hydrogen from Water**

Hydrogen can be obtained from the "splitting" of water into its two basic components of hydrogen and oxygen. At present, the only practical method for this is a process called electrolysis.

Electrolysis involves passing an electric current through water. The current enters the electrolysis device through the cathode—a negatively-charged terminal, passes through the water, and leaves through the anode—a positively charged terminal. Hydrogen is separated and collected at the cathode and oxygen is separated and collected at the anode.

Electrolytic hydrogen is relatively expensive, with 80% of the operating cost being the cost of electricity. The method is economically feasible for uses requiring small amounts of hydrogen or when power costs are low. Also, the hydrogen product is very pure and can be used in the pharmaceutical, electronics, and food industries.

Hydrogen can also be obtained from water by a variety of other methods which are not currently feasible for large-scale production, but are the targets of research and development activities. These include photoconversion, which uses biological organisms or synthetic material to split water, and photoelectrochemical processes, which use semiconductors to generate an electric charge to cause the water splitting activity.

Hydrogen's EXPANDED role as an energy carrier will more than likely be as a fuel for surface transportation. Transportation contributes significantly to air pollution, especially in highly populated urban areas, and is presently one of the most inefficient uses of energy, with a total conversion efficiency of 13% to 18%.

Hydrogen will probably be used initially as an additive to existing fossil fuels for surface transportation. Hydrogen can be combined with gasoline, ethanol, methanol, and natural gas for

fueling internal combustion (IC) engines, resulting in reduced pollution and increased performance.

Remarkably, just adding 5% hydrogen to the gasoline-air mixture in an IC engine could reduce nitrogen oxide emissions by 30% to 40%. An IC engine converted to burn only hydrogen produces water and minor amounts of nitrogen oxides as exhaust. As with other fuels, firing hydrogen in an IC engine emits small amounts of carbon dioxide and hydrocarbons because of the incidental burning of lubricants.

A near-term opportunity for hydrogen power in vehicles may be presented by recent California legislation requiring that 10% of new cars offered for sale within the state be non-polluting vehicles by 2003. The ZEV standards could be met by electric vehicles with electricity generated by onboard hydrogen-powered fuel cells, as well as by battery-powered electric vehicles that have already been introduced on a lease basis in California.

In addition to surface transportation, air transportation is an attractive future application for hydrogen. The high energy content per unit of weight of liquid hydrogen makes it an attractive aircraft fuel. It offers noticeable savings in fuel consumption and in aircraft weight when compared with current jet fuel. These advantages are particularly significant for supersonic aircraft. Because air transportation has a unique and dedicated energy infrastructure, conversion to hydrogen would be much less complex than a similar transition in the area of ground transportation.

Mid-term opportunities, within 10 to 13 years, will involve the use of hydrogen in electric utility power generation. Initial uses could include supplemental blending of hydrogen with natural gas for electricity generation to reduce emissions. Longer term, hydrogen-powered fuel cells could provide on-site electricity generation for remote commercial and residential locations. Hydrogen could also be produced by renewable sources, such as wind power and photovoltaic installations, for energy storage and reversion to electricity to be used when the intermittent renewable sources are not generating power.

These expanded uses of hydrogen in energy will depend upon more research and development to identify and overcome economic and technical barriers.

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#### **Fuel Cells**

Fuel cells are devices that convert hydrogen gas directly into low-voltage, direct current electricity. The cell has no moving parts and works on basic electric principles.

The process is essentially the reverse

### Multi-Quad Objectives

A "quad" is a unit of thermal energy which is often used to measure total energy generated and consumed in the economy. A quad is equal to one quadrillion ( $10^{15}$ ) British thermal units (Btu's), or 1.055 exajoules, and is the amount of energy consumed by 1 million U.S. households. The primary objective of the DOE Hydrogen Program is to develop hydrogen technologies to the point that they will allow hydrogen to replace energy derived from fossil fuels. Demand goals for the Program, therefore, are established in quads of fossil-fuel derived energy rather than in cubic feet of hydrogen gas.

### PRODUCTION TECHNOLOGY ADVANCES

Advances in hydrogen production technology have the potential for creating significant improvements in the infrastructure necessary for widespread hydrogen use. Production technology is less advanced than technologies in storage and utilization systems, and has the greatest potential for reducing total costs. Critical issues in developing hydrogen

energy are hydrogen's high cost of production and the selection of the best feedstock and production process.

Production research is focused on technologies that have moderate to high potential for overcoming cost and energy source barriers. There are active research and development projects for photoconversion methods such as photobiological and photoelectrochemical systems, and thermochemical processes such as gasification and pyrolysis. These technologies are in the early research and development stages, but have strong potential for being cost-effective production systems. These processes use renewable sources of energy for hydrogen production.

The photoconversion production of hydrogen uses as its resource base solar energy—in the form of sunlight—and water. The production system uses energy from sunlight to dissociate, or

### Growing Interest in Hydrogen

While its potential as an energy carrier and fuel has been recognized for many decades, the current level of interest in hydrogen energy dates from the early 1970's. The international oil embargo by the Organization of Petroleum Exporting Countries (OPEC) sent energy awareness shocks throughout the world, creating major concerns about energy independence and fuel shortages. The cost of gasoline rose during the decade and the availability of natural gas appeared limited, with reserves shrinking.

Certain scientists became aware that hydrogen could play an important role in the energy

split, water into hydrogen and oxygen. This process uses light energy without going through the separate electric generation step required by electrolysis. Photoconversion couples a light-absorbing system with a water-splitting catalyst—a substance to initiate or speed up a chemical reaction.

There are two primary classifications of such systems, photobiological and photoelectrochemical. In the photobiological processes, chlorophyll, contained in living plants, is the light-absorbing material, and an enzyme is the water-splitting catalyst. In the photoelectrochemical system, also referred to as photoelectrolysis, a semiconductor is the light-absorbing material and a metal is the catalyst.

Thermochemical production processes use heat to produce hydrogen from various sources, including natural gas and gases derived from coal, solid waste, and biomass. Production from biomass either by gasification or pyrolysis holds considerable promise among technologies that derive hydrogen from renewable energy sources.

## **Production Using Photobiological Technology**

Photobiological processes for hydrogen production involve the generation of hydrogen from biological systems, generally using sunlight. Certain algae and bacteria can produce hydrogen under specific conditions. Pigments in algae absorb solar energy, and enzymes in the cell act as catalysts to split water into its hydrogen and oxygen components.

Research and development is in progress to better understand the detailed mechanisms in these biological systems. However, these programs are in early stages of research and development and energy conversion efficiency—the amount of hydrogen energy produced as a percent of incident sunlight energy—is low, at about 5%. These processes require advances in efficiency and reductions in anticipated capital costs to become viable methods for producing hydrogen on a broad scale.

Research is focused on two approaches: whole-cell systems involving bacteria, and cell-free systems that isolate and use just the hydrogen-producing enzymes. The whole-cell systems have potential for near-term production at solar conversion efficiencies of 5% to 10%, whereas the cell-free systems have promise for more long-term technologies that may produce efficiencies of greater than 10%.

In addition to problems with low conversion efficiencies, nearly all enzymes that break out hydrogen are also seriously inhibited by the presence of oxygen, a key component of water splitting. There is also the problem of regenerating the systems to extend production periods and improve production stability.

There are several research activities in place to address these concerns with photobiological production processes, including:

- Near-term identification of bacteria and development of a system that can produce hydrogen from synthetic gas at ambient temperature and pressure in darkness. More than 300 strains of this unique type of bacteria have been isolated from natural sources.
- Creation of a strain of a hydrogen-producing microbe that is tolerant of oxygen. Currently, six oxygen-tolerant bacterial strains have been identified that also produce hydrogen.



Research is focusing on genetic transfer of these enzymes to create stable hydrogen-producing strains of algae.

- Development of a cell-free system that will spatially separate hydrogen-producing enzymes from oxygen-producing enzymes with a solid surface. The physical separation will overcome the oxygen-tolerance problem, and cell-free systems have the long-term potential to reach energy conversion efficiencies of nearly 25%.
- Extension of hydrogen production periods in batch or continuous cultures to periods of months rather than the current production periods of days or weeks.

### **Production Using Photoelectrochemical Technology**

The photoelectrochemical process uses semiconducting electrodes in a photoelectrochemical cell to convert optical energy into chemical energy. There are essentially two types of photoelectrochemical systems—one using semiconductors and another using dissolved metal complexes.

In the first type, a semiconductor surface is used to both absorb solar energy and to act as an electrode for splitting water. This technology is still at an early stage of development, although energy conversion efficiency has increased from less than 1% in 1974 to more than 8% at present. Even higher efficiencies have been obtained with the addition of an external electric charge to help drive the chemical reaction.

Operating lifetimes of these systems are limited because of the light-induced corrosion of semiconductor materials and other chemical effects. Current research is focused on improving cell energy conversion efficiency and lifetime, and reducing costs. Projects are active in the following areas:

- Identifying new semiconductor materials with high conversion efficiency and stability. At present, the material with the highest efficiency is a compound—known as *p*-type indium phosphide—that acts as a semiconductor. The most stable photoelectrode is titanium dioxide; however, this material has a conversion efficiency of less than 1%. Both of these materials require some external voltage to aid in the water-splitting reaction. Other

materials, which require no external electricity, are being studied, including indium gallium phosphide, amorphous silicon, stable organic semiconductors, and various new semiconductor alloys.

- Researching new approaches to reduce corrosion. One of the more promising methods is to use ultra-thin layers of protective material on the electrode surface.
- Incorporating multiple layers and sensitized dyes to maximize solar absorption and conversion to hydrogen. Such a design mimics the action of photosynthesis where multiple photoconversion systems function together to enhance sunlight energy to drive chemical reactions. Investigations are proceeding in the areas of low-cost systems, multiple layers of organic dyes, and thin-film semiconductors.

The second type of photoelectrochemical system uses dissolved metal complexes as a catalyst. The soluble metal complex absorbs energy and creates an electric charge separation, which drives the water-splitting reaction. Researchers are focusing on identifying catalysts that can more efficiently dissociate water and produce hydrogen. This method is currently less advanced than the semiconductor processes, but offers the prospect of avoiding corrosion problems.

### **Production by Gasification or Pyrolysis of Biomass**

Applying heat to coal, municipal solid waste, and biomass—wood, grasses, and agricultural waste—produces several different gases, including hydrogen. The composition of the gases depends on the type of feedstock, the availability of oxygen, the temperature of the reaction, and other parameters. Hydrogen in the gas can range from a small percentage to the majority of the gas, varying the heating value by as much as a factor of five.

Renewable hydrogen research is currently focused on medium-heating-value gas from biomass for use as a fuel or chemical gas feedstock. Gasification of biomass uses either waste or dedicated feedstocks, such as grasses or trees grown specifically as an energy source. Biomass gasifiers have been developed using fixed-bed, fluidized-bed, and entrained-bed combustion technologies.

An important environmental advantage of using sustainably grown biomass as a hydrogen feedstock is that the carbon dioxide—a principal climate-changing emission—emitted in biomass

conversion contributes no increase in total carbon dioxide in the atmosphere. Carbon dioxide is consumed by the biomass while growing, and the conversion process only returns the same amount of carbon dioxide back to the air.

For biomass to become a cost-effective source of hydrogen, significant research advances must be made. Techniques for separating and purifying the hydrogen by use of selective membranes or catalytic processes must be improved. More efficient concepts for gas cleanup— the removal of tars and oils—need to be evaluated. A high priority of research is to focus on an advanced catalytic gasification concept to determine performance when the gasifier is run continuously.

An alternative method of producing hydrogen from biomass is a combination of pyrolysis and steam- reforming processes. Pyrolysis is the process of using heat to break apart complex molecules into simpler units. Applying this to biomass generates reactive vapors, which then can be converted to hydrogen, carbon monoxide, and carbon dioxide using steam in a catalytic environment. This process has the potential for being one of the least expensive production technologies, but it is at an early stage of research. Researchers are focusing on identifying optimum catalysts for the steam-reforming step, and on evaluating the economic feasibility and environmental sustainability of the total process.

### ***FUTURE STORAGE TECHNOLOGIES***

Cost-effective storage systems are critical to the widespread use of hydrogen as a viable energy option. Current storage methods are too expensive and do not meet the performance requirements of the various applications. This is especially true for hydrogen's potential use as a transportation fuel, where there is a need for high energy density—energy content per unit of space—and lightweight mobile storage. At normal temperature and pressure conditions, hydrogen has an extremely low energy density, about 1/3300 that of gasoline. A strategic long-range storage goal for transportation is to achieve weight and volume storage densities comparable to gasoline.

Volume density and weight are not such critical factors for utility and other stationary applications; rather, storage efficiency—energy losses due to the storage process—and system costs are the major considerations.

An economic, practical hydrogen storage system depends on capacity, structural integrity of the storage material, total cost, and conditions required for storage, including temperature, pressure, and purity of hydrogen. Research into future storage technologies focuses on **physical storage** in a compressed gas or liquefied state, and **solid-state storage** using gas-on-solid adsorption in materials such as high surface-area carbon, or absorption in the interstices of a metal hydride.

### **Research in Physical Storage Systems**

Storage of hydrogen in the form of compressed gas and cryogenic liquid—storage at extremely low temperatures—is practical and available today. But current technology is not practical for widespread energy use. Cryogenic liquid hydrogen requires significant energy consumption for the liquefaction process, and it is expensive. Compressed gas is stored at 14 to 17 megapascals (MPa) (2000 to 2500 pounds per square inch [psi]) and currently requires large, heavy containers.

Research is directed toward improving these existing technologies, and some promising results are coming from the use of new, lightweight graphite composite material developed for aerospace projects. This material has the potential for providing high-pressure—up to 41 MPa (6000 psi)—hydrogen storage in lightweight containers for transportation applications. Additional research and safety testing is required to develop practical, safe, and reliable storage systems using these new materials.

### **Advances in Solid-State Storage Methods**

Solid-state storage—gas-on-solids and metal hydrides—are safer technologies and store more hydrogen per unit volume than physical storage. They are also more expensive and heavier. Research and development of solid-state methods has focused on determining the hydrogen adsorption/desorption properties of commercially available carbons and zeolites. In order for high-performance storage materials to become a reality, a more complete understanding of the fundamental mechanisms of solid-state storage is needed. Specific research is planned or being conducted on:

- Determining current and theoretical hydrogen storage capacities, rates of charge and discharge, accompanying thermal and mechanical effects, and costs of available materials.

- Establishing the capability to manufacture conventional solid-state hydrogen storage materials, such as magnesium-based hydrides and high-surface-area activated carbon.
- Investigating new materials systems, such as fullerenes, a form of carbon; porous silicon; porous metal-silicides; zeolites; dihydrides and non-classical polyhydrides; transition metal and dichalcogenides; hydrogenated amorphous alloys; metal hydride thin-films; new synthetic methods; and highly porous and nanostructured materials.
- Working with the geodynamics of underground storage; compatibility with existing natural gas storage facilities; and technology to lower the cost of liquefaction, such as magnetic refrigeration.

***Gas-on-Solids Adsorption Technology***—Hydrogen can be stored by being adsorbed onto the surface of activated carbon in a method known as gas-on-solid adsorption. The volume density of this method can actually be higher than compressed gas storage, although weight and energy efficiency of the total storage system may not be as great. The adsorption of hydrogen on carbon under low temperature—150 K (-190 F)—has emerged as a promising storage alternative from the space program.

This technology has potential for both stationary and mobile storage applications. The weight and volume densities are comparable to liquid hydrogen systems and additional improvements are possible. Work is being done to improve knowledge about micropore filling mechanisms, which could lead the way to improving storage capacity.

***Metal Hydride Technology***—Certain metals have the ability to absorb and retain hydrogen under specific temperature and pressure conditions and then release the gas under different conditions. When containing the hydrogen, these metals are called metal hydrides. Magnesium is one of the metals most commonly used in this process.

Hydrides are safe and have high volume density, but are currently expensive compared with compressed gas or carbon adsorption storage systems. Low-cost hydrides that can store large amounts of hydrogen require high temperatures to release the hydrogen. On the other hand, hydrides that release hydrogen at lower temperatures are more costly and provide less storage capacity.

Key factors in developing practical, economic hydride systems are the type of hydride used, the desired operating temperature, the desired capacity, and various system component costs such as packaging and heat exchangers. Hydride systems must demonstrate long life under repeated loading and unloading cycles without significant loss in storage capacity. Capacity can also be adversely affected by trace amounts of impurities in the hydrogen.

Research is addressing all of these factors. One new direction showing potential for practical application is the use of polyhydride complexes using cobalt and other transition metals. Research indicates that these materials have higher storage capacities and faster recycling times than other hydride systems tested.

### ***TRANSPORT***

Hydrogen must be transportable to be effective as an energy carrier. A cost-effective and efficient delivery infrastructure is needed to move it from its point of production to its point of use. Current methods of delivery are by pipeline, truck, rail and barge. Technologies must stress safety, efficiency, and cost-effectiveness. A primary focus of research and development in this area is on determining the feasibility of using the existing natural gas pipeline network for large-scale hydrogen transport.

### ***UTILIZATION***

Many uses of hydrogen are long-term in nature and will depend on technological advancements in the areas of production, storage, and transportation. The most near-term application is expected to be in transportation, either as a fuel additive, as fuel for IC engines, or for fuel cell/electric vehicles. Because many of the technologies for widespread hydrogen use have yet to be developed, research and development of utilization technology is somewhat limited. The current utilization research is focusing on more near-term applications that will be part of the transition from a fossil-fuel economy to a hydrogen-based energy economy.

A key use of hydrogen in the transition economy will be in reciprocating IC engines to meet near-zero emission goals. Research and development projects are identifying practical mixing, ignition, and combustion conditions, and optimizing the use of hydrogen and hydrogen mixed with methane in IC engines to be used in conventional and hybrid vehicle configurations.

An integrated IC engine/delivery/storage system with efficiencies approaching 45% and addresses safety and certification issues of hydrogen use in transportation is a current development goal.

Research is also being conducted at a theoretical level to better understand the complex processes that take place in IC engines operating on hydrogen and hydrogen combined with hydrocarbon fuels. Computer models developed in this effort will hopefully allow the design and manufacture of new, more energy efficient, and cleaner engines to run on these fuels.

## **SYSTEM STUDIES**

System studies are conducted in parallel with research and development activities and are used to evaluate the various possible scenarios for integrating hydrogen into the economy. These studies include analyses of technologies and processes and the definition of infrastructure requirements of a hydrogen-based economy.

Study results provide guidance to ensure that the research and development investment is directed to those systems and technologies with the best possibility of being implemented. System studies address life-cycle cost analysis, system safety concerns, reliability issues, environmental analysis, and market analysis and assessment.

***Life-Cycle and Energy Pathway Analysis***—In judging the efficiency and economy of any energy source or carrier, it must be evaluated within the context of its total life-cycle. This includes complete costs and benefits for all aspects of all components of the energy system of which it is a part. An energy system considers economic and environmental costs and energy efficiency, from production of the primary source of energy to final end-use.

Several analytical methods, particularly the Energy Pathway Analysis model, are helping to create a balanced portfolio of research and development projects that reduce risk and increase the potential for successful implementation of hydrogen technologies. These analyses will be used to define costs and economic barriers and benefits related to the utilization of hydrogen as an energy carrier. The results will identify the infrastructure and institutional changes needed to introduce the technology.

***System Safety Factors***—A common perception is that hydrogen is a dangerous fuel, while, in fact, it is not any more hazardous than other fuels currently in common use. Research and

development is used in evaluating system safety as a technological risk factor, focusing on the following areas:

- Hydrogen, like natural gas, is odorless and must have an odorant added so that it can be detected by the average person in the event of a leak.
- A hydrogen flame is virtually invisible when it burns, except in situations of very low background lighting, and must have a luminant added to make the exposed flames visible.
- Both the odorant and luminant must be effective in low concentrations, be compatible with hydrogen energy systems, and not compromise emission performance.



## Energy Pathway Analysis Model

An Energy Pathway Analysis model for measuring total economic and environmental costs of an energy system has been developed. This model measures and compares capital costs and emissions for each segment of the system. The analysis indicates specific areas of technology where development and cost reduction are critical to the effective implementation of hydrogen as an energy carrier. The model highlights areas where hydrogen is most effective in reducing climate changing emissions as compared to a fossil-fuel system.

An energy pathway model can be established for any specific combination of energy sources and end uses. As energy progresses along a pathway, there are energy losses at each transformation process. Some energy conversions in the pathway are more efficient and a greater percentage of the total energy available is carried to the next phase. Others are less efficient, resulting in significant declines in energy along the pathway. All of these factors can be evaluated and presented in a summary reflecting estimated costs and environmental affects of an energy system.

As shown in the accompanying examples, we can see the respective costs and emissions associated with some of these pathways. Each model is scaled to produce one energy unit to the consumer; in these models, that energy unit is defined to be one kilowatt hour (kWh). The vertical bars represent the energy required at each transformation step to deliver one unit of energy to the user.

For the crude oil to transportation model, for example, a constant supply of 9.5 kWh of energy is required to deliver 1.0 kWh of energy to power a vehicle. The percentages in the example represent the level of efficiency at each step. In the direct solar/hydrogen/electricity example, 11.6 kWh of energy is required to produce 1.0 kWh of delivered energy. This energy requirement is derived from sunlight and is, therefore, essentially "energy free," meaning there is no constant input of energy required to produce the initial energy source.

With this basic framework established, the model can then add economic and environmental considerations. At present the models include capital investment required at each step per unit of energy; in the future, operating and maintenance costs will also be included. Again, the renewable energy pathways are unique. When compared with fossil fuel plants, renewable generating systems require greater installed generating capacity to produce equivalent energy output.

Emissions are estimated for each step of a pathway, giving an approximation of total pollution emitted in the form of carbon dioxide, nitrogen oxides, and sulfur dioxide. Capital investment for renewable/hydrogen systems are currently expected to be more expensive per unit of energy, but the systems will be emission free. Production costs and "external" environmental costs must also be factored into any economic comparisons of these systems.

***Reliability of Systems***—Hydrogen systems must be at least as reliable as current, conventional energy systems. Developing hydrogen technologies and materials to provide greater reliability than the present fossil fuel infrastructure will contribute to the more rapid application of the hydrogen alternative. The energy pathways model will be expanded and further developed to include a reliability assessment of the pathway options.

***Environmental Analysis***—Hydrogen as an energy carrier has several environmental advantages over conventional fuels, including the abundance of a clean source in water and the potential for reducing the carbon dioxide, sulfur oxides, and nitric oxide emissions that result from the use of fossil fuels. Analysis evaluates the technical and economic effects of state and federal legislative actions to promote and protect a cleaner environment and to reduce global climate changes. Environmental issues are studied in regard to hydrogen use as an energy carrier.

***Market Analysis and Assessment***— Identifying stakeholders most likely to be affected by the transition to a hydrogen energy system, and determining how hydrogen can be introduced to their business plans and operations are all a part of market analysis. These studies include information exchange with participants in the utility, chemical, petroleum, and transportation industries; trade and professional associations; and insurers.

## THE FUTURE OF HYDROGEN

Since hydrogen's potential as an energy carrier emerged during the energy crisis of the 1970's, the vision of a hydrogen-based energy economy has seemed to outpace the realities of hydrogen energy technology. Substantial advancements are required in technologies for hydrogen production, storage, transport, and utilization before this future can be achieved.

Hydrogen systems must be competitive with other energy alternatives in economic, efficiency, and environmental benefits before they will achieve widespread use and become the basis of a renewable, sustainable energy future. By focusing on the role of hydrogen energy as a transition between fossil-fuel dependence and the widespread adoption of renewable resources, hydrogen can be integrated into the national energy picture as rapidly as is economically and technically feasible.

### Hydrogen Technical Advisory Panel

Under the directive of the Matsunaga Act, the DOE formed the Hydrogen Technical Advisory Panel (HTAP) in 1990 to facilitate the development of hydrogen as an energy carrier. The Panel acts as an advisory board to the DOE Program management, and is composed of representatives from industry, universities, financial institutions, and environmental organizations.

The Panel is directed to specifically review and make recommendations in the following areas:

Implementation and conduct of the Program  
Economic, technological, and environmental consequences of deploying hydrogen energy systems  
The hydrogen multiyear program plan

At its creation, the Panel developed the following Consensus Vision to drive its work in this area:

"Hydrogen will join electricity in the 21st century as the primary energy carriers in the nation's sustainable energy future. Both energy carriers will ultimately come from renewable energy sources, although fossil fuels will provide a long-term transitional resource. Future hydrogen suppliers will deliver a significant portion of America's energy for transportation and other applications. For these applications, hydrogen offers a non-polluting, inexhaustible, efficient, and potentially cost-effective energy system derived entirely from domestic energy sources."

As technical and economic barriers are overcome, the future of hydrogen as an energy carrier is promising in several areas:

- Hydrogen mixed with fossil fuels to significantly reduce pollution from vehicles and natural gas-fired power plants
- Hydrogen powered fuel cells to provide non-polluting power for vehicles and stationary power generators

- Hydrogen as an energy carrier to make intermittent renewable resources a viable component of the national electricity grid

Significant advances in renewable energy technology and hydrogen technology may even create stand-alone, distributed power centers, with renewable systems generating electric and hydrogen power for individual homes, buildings, and office parks. Long-term commitment to research, development, and demonstration programs will help hydrogen achieve its full potential as an energy carrier of the future.



# HANDLING HYDROGEN SAFELY

## Hydrogen is a Part of Life

Users of hydrogen are as varied as today's global marketplace. Hydrogen is a key component in the manufacture of chemicals especially ammonia and methanol. It is used in large quantities in refineries for manufacturing gasoline and heating oil. It is used to make fertilizers, glass, refined metals, vitamins, cosmetics, semiconductor circuits, soaps, lubricants, cleaners, margarine, peanut butter and rocket fuel. Hydrogen fuel holds much promise for a future in which everyone can have energy that is efficient and clean. The properties of hydrogen are well known to a variety of producers of consumer goods and services, and understanding the special properties of hydrogen is necessary for its safe use. Can hydrogen be safely handled? To thousands of industrial consumers the answer is yes.

Millions of pounds of hydrogen are used daily in production plants across the country and around the world (50 million pounds daily in the U.S. alone). The National Aeronautics and Space Administration (NASA) is the largest user of liquid hydrogen in the world. But the public's impression of hydrogen is often the consequence of one well-published incident the Hindenburg. In fact, the Hindenburg did not explode: it did, tragically, catch fire. In 1937, when the accident occurred, the practice was to allow the hydrogen to be stored in highly combustible materials, a practice which current safety regulations do not permit.

What is often not acknowledged about the Hindenburg tragedy is that because hydrogen dissipates quickly, no Hindenburg fatality was the result of a burn from hydrogen.

Most hydrogen today is derived from light hydrocarbons or ammonia, the electrolysis of water, or taken as a by-product of petroleum production and chlorine manufacture. It is distributed by pipeline, over-the-road trailers and rail and barge, via small portable containers.

The following information is not a guideline for establishing equipment designs or operating procedures. Information of this type is available in numerous regulations, standards, industrial data sheets and technical publications mentioned later.

Hydrogen can be handled safely when guidelines for its safe storage, handling and use are observed. Hydrogen is a fuel. To be a fuel it must have combustible properties. Hydrogen's combustion properties warrant the same caution any fuel should be given, and some cautions which are unique to hydrogen.

## **HYDROGEN IS A FUEL**

Hydrogen, in its liquid form, has been used as a fuel in space vehicles for years. Hydrogen has a high combustion energy per pound relative to any other fuel, meaning hydrogen is more efficient on a weight basis than fuels currently used in air or ground transportation. This weight factor makes hydrogen an attractive fuel.

Hydrogen is both flammable and buoyant. It is flammable over a wider range of concentrations than either gasoline or natural gas, but due to its buoyancy, it dissipates more rapidly than either of these fuels in a spill. Hydrogen gas, like other gases used today, should be used in areas that can be ventilated.

Hydrogen can and has been used safely when guidelines for its proper handling and storage are observed. Individuals who work with hydrogen systems are trained in hydrogen's safe handling and use by observing precautions like: preventing hydrogen leaks, taking proper action if leaks occur, eliminating the opportunity for leaked hydrogen to accumulate and eliminating sources of ignition.

Hydrogen fuel is unique. It is clean. Its primary combustion by-product is clean water vapor. Hydrogen is versatile. It can be used in applications requiring electricity or gas, and it can link the fossil-based energy supply of today with the renewable energy tomorrow.

As the cost of hydrogen comes down and its availability increases, interest in its use as a fuel will intensify. Therefore public awareness of hydrogen safety is essential.

## **HYDROGEN "TOWN GAS" ONCE LIT AMERICA**

In towns and cities all across America, lamplighters once lit gas street lights at dusk. Inside middle class homes, gas lamps provided light and gas heaters provided warmth. The gas that fueled the lights and furnaces was not the natural gas of today, but a hydrogen-rich mixture called "town gas" Town gas was manufactured from coal and typically contained 50% hydrogen, 50% carbon monoxide and trace amounts of other gases like methane.

Once vast natural gas fields were discovered, long-distance pipelines were laid linking the producing states of the Southwest and Gulf to the consumer states in the Northeast and Midwest. Utilities stopped manufacturing town gas and switched to the more convenient natural gas. Today, more than 1.2 million miles of natural gas pipeline criss-cross the U.S.

Delivery of town gas is rare today, but delivery of pure hydrogen gas is not. Approximately 700 miles of hydrogen pipeline exist in the U.S., Germany and England. This is small compared to natural gas systems, but it is important to note that there are hydrogen pipelines

in operation today that deliver gas to the user successfully.

From the town gas experience of the past, to the hydrogen gas experience of today, a solid foundation of knowledge has been established on how to handle hydrogen safely.

### Experience Counts

The U.S. space program's use of liquid hydrogen began in the 1950's, and demand for hydrogen worldwide continues to grow. Industry has consistently demonstrated its ability to safely produce, ship and handle hydrogen as a gas as well as in liquid form.

NASA's experience with the safe use of hydrogen began over four decades ago and it continues to prove that experience using hydrogen can lead to impressive applications that will favorably impact our future economy and environment. Not only is hydrogen the major propellant used in space flight, but hydrogen fuel cells on board the space shuttle power life support systems and computers, and create drinkable water as a by-product.

In a report prepared for the Department of Energy, Factory Mutual Research Corporation of Norwood, Massachusetts, compiled a data bank of hydrogen accident reports in order to analyze the information and anticipate common hazards associated with hydrogen use. The study shows a multitude of hydrogen uses dating back to 1965, and its safety record is a good one. With the use of hydrogen among a wide range of applications, experience with handling hydrogen in its different forms is long standing. This report, along with many others, has helped form the conclusion that hydrogen, handled properly, will be a safe alternative to fossil fuels.

## COMMITTED TO HIGH STANDARDS

People involved in the manufacture of equipment know the standards for the design of hydrogen systems, and individuals who work with these hydrogen systems are familiar with safe handling procedures. This knowledge is developed through training in the operation of the complete system, understanding the properties of hydrogen and observing the necessary safety precautions involved in hydrogen production, handling and use.

Many organizations are concerned with hydrogen safety. Over the years, much effort has gone into the preparation and publication of guidelines and requirements for hydrogen systems and equipment. The National Fire Protection Association publishes guidelines for storage systems. The Department of Transportation regulates the distribution of hydrogen over the nation's roads. Associations like the American National Standards Institute and the American Society of Mechanical Engineers publish standards for components used in hydrogen equipment. The Compressed Gas Association sets standards for many gases including hydrogen and their materials cover gas production, handling



and use.

The standards set by these organizations are high. It is industry's long standing commitment to these high standards that enables hydrogen to be safely handled and used today, and gives the needed experience and knowledge for the future.

### **SUMMARY**

The potential is great for the widespread use of hydrogen in the transportation and residential areas and as a carrier and storage medium of energy. Global environmental concerns and future limitations in the availability and use of hydrocarbon products continue to encourage consideration of hydrogen in a variety of applications.

Hydrogen safety continues to be of utmost importance not only to those working routinely with hydrogen, but to the general public as well. Hydrogen handling has had an excellent safety record. This is due to the use of proper safety precautions, familiarization with hydrogen properties, and strict adherence to rules, regulations and standards established through years of experience and research.

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