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ELECTROLYSIS-BASED HYDROGEN STORAGE TECHNOLOGY

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ABSTRACT

Production and storage technology pertinent to the Hydrogen Program at Brookhaven National Laboratory is briefly described. The major development areas deal with advanced water-electrolysis systems, hydrogen storage materials and systems, and end-use applications. Related work by organizations having contracts managed by BNL is included. Work on hydrogen production deals with improving the system for KOH electrolysis, and on developing the acidic solid-polymer-electrolyte system for the electrolysis of water. The advantages of and techniques for storing hydrogen via metal hydrides and hollow glass microspheres are described. TiFe-based hydride has been tested as an energy storage medium for electric energy storage, for automotive fuel, and for bulk hydrogen storage. Pairs of selected hydrides have been used in tests simulating a solar-driven heat pump. The pressure-temperature characteristics of hydrides are being utilized in development of a hydrogen chemical compressor. Glass microspheres are being studied for the automotive fuel application.

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INTRODUCTION

The scope of this paper is limited to hydrogen technology pertinent to the program at Brookhaven National Laboratory (BNL). The major development areas of this program deal with advanced water-electrolysis systems, hydrogen storage materials and systems, as well as end-use applications. Work in these areas is conducted both at BNL and at organizations having contracts managed by BNL. Numerous individuals have contributed to the technology. The overall objectives of the program are to develop the technological base for promoting the entry of hydrogen to the energy infrastructure, and to identify the technology which is suited for transfer to the private sector.

Although most hydrogen is now produced and consumed locally as an essential chemical feedstock, there is an increasing interest in its use as a secondary energy carrier because it is environmentally desirable and is a flexible fuel form. There is an ample supply of water for producing electrolytic hydrogen, and the water resulting from combustion closes the cycle. Energy to produce hydrogen is available from inexhaustible energy resources: solar in its various forms, geothermal, and nuclear. Those that are of an intermittent nature are easily accommodated by hydrogen because it can be used to supplement natural gas, to power a variety of engines, to provide electrical energy via the fuel cell, or it can be stored for later use. Also, its gravimetric energy density is much higher than that of other fuels. Thus, hydrogen is a versatile and desirable option for energy resource conversion.

Before hydrogen can be widely used on a large scale, its cost will have to be close to that of common fuels, and a comparable infrastructure established. Such use now appears to be several decades away. In the interval there will be increasing demands for hydrogen where pollution reduction is essential. As new uses arise for hydrogen, various supply, distribution and storage systems will be

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required. In preparation for satisfying future demands, the Department of Energy, through the Division of Energy Storage Systems, is supporting modest development efforts to establish a technology base.

ADVANCED ELECTROLYTIC PRODUCTION

One of the two techniques under development consists of electrolyzing 20-30% KOH solutions. Improvements (efficiency >55-75%) in this established technology are being sought by substantially increasing the operating temperature above 80°C and by adapting the design to operating pressures in the vicinity of 20 atm so that for some applications a compressor is not needed. Teledyne Energy Systems is performing this work in cooperation with BNL. More resistant anode and cathode electrocatalysts and separator materials are being sought to withstand the increased corrosion at temperatures in the vicinity of 120°C. TES has set up a test fixture for evaluating candidate materials and measuring cell voltage phenomena as a function of current density, temperature, operating pressure and time. A five-cell bipolar module is used in a filter-press arrangement; it is similar to industrial designs so that the results may readily be applied to larger cells. Supportive work at the University of Virginia is concerned with determinging the cause of time-dependent energy losses and evaluating possible solutions. The advanced systems under test at TES demonstrate improved efficiency: 80-85% at 377 mA/cm^2 (350 A/ft^2) whereas the goal is 90% at 538 mA/cm^2 (500 A/ft^2). TES is developing a plant-scale electrolyzer (0.765-M^2 or 8.25 ft^2 electrodes) on their own.

The second technique is based on technology originally developed by the General Electric Company for fuel cells used on space craft. The electrolytic cell uses an acidic solid polymer electrolyte (SPE), electrode structures, and distilled water, in a bipolar filter-press arrangement. It offers higher efficiency and current density, as well as higher operating pressures (34 atm), than the alkaline electrolyzer. The present efficiency is near 80% at 1076 mA/cm^2 (1000 A/ft^2) whereas the goal is 90%. Development has progressed to testing a 50-kW 12-cell module having cell areas of 0.232 M^2 (2.5 ft^2). BNL is assisting with the selection and evaluation of suitable low-cost materials, and Brooklyn College is performing fundamental investigations on anode electrocatalysts.

Plans for scaling up the GE system are well under way. The present cell size will be demonstrated at the 200-kW level, and modules having cell areas of $0.928M^2$ (10 ft^2) are under consideration. Support for the program is also provided by utility-related organizations and GE.

HYDROGEN STORAGE MATERIALS AND SYSTEMS

Hydrogen is now routinely stored as a compressed gas or cryogenic liquid, and more recently as decomposable metal hydrides in the form of particulate solids. Certain metals and alloys react with hydrogen in a reversible manner at modest pressures (<34 atm) and conveniently serve as compact storage media. The heat of formation must be removed to sustain the charging reaction and an equivalent amount supplied to discharge the hydrogen. Several practical hydrides discovered at BNL and their practical hydrogen contents are: $FeTiH_x$ (1.5 wt %), $TiCr_{1.8}H_x$ (∿3 wt %), Mg_2NiH_x (∿3 wt %) and MgH_x catalyzed with 10 wt % Ni (5.5 wt %).

Their pressure-temperature-composition properties vary over a wide range. The most widely used hydride, $FeTiH_x$, or a Mn-substituted version $TiFe_{0.9}Mn_{0.1}H_x$, functions at ordinary temperatures, 0-100°C. Much of the technology for producing hydride-grade alloy on an engineering scale was performed by the International Nickel Company, and its subsidiary MPD Technology Corp., in cooperation with BNL. The Cr-containing hydride and its Mn derivatives are very unstable and more useful for their pressure characteristics. Temperatures in the vicinity of 300°C are required for functioning of the Mg-based hydrides and for this reason they have received less attention. Efforts are under way at Air Products and Chemicals Corp. to modify the system for use at lower temperatures.

Hydrides are used in pressure vessels provided with some form of heat exchanger and porous metal filter/distributor tubes. In cylindrical vessels, U-tube heat exchangers have been used or the hydride has been canned and water used externally. Embossed heat-transfer panels are also suitable. For energy-storage systems transfer times of 5-10 hours pose no unusual problems, but for transfer times in the range of ten minutes or less, some form of heat-transfer enhancement is required.

Tests with TiFe-based hydride containers have shown that they are much safer than a compressed gas cylinder, a liquid propane cylinder, or a gasoline tank. The energy release rate is much slower and the effects considerably less dramatic when the tanks are punctured.

A novel concept for storing hydrogen at a pressure of 400 atm in glass microballoons is being developed by Robert J. Teitel Associates. The principle is based on the wide variation in hydrogen permeation rate as a function of temperature. Loading is done at 300°C and the leakage rate at ambient temperature is very low. A recent demonstration showed that 10 wt % loading is practical and that at 200°C hydrogen could be evolved at a rate several times that required for an automobile engine. Projections indicate that this system will be lighter in weight and lower in cost than hydride systems.

The bulk storage of hydrogen in underground cavities is being assessed by the Institute of Gas Technology.

APPLICATIONS

Hydrides have been used successfully in a variety of applications. One of the first involved the storage of off-peak power by electrolyzing water and storing the evolved hydrogen as $FeTiH_x$ until the energy was used in a fuel cell to regenerate power. A variety of cars and buses have also used this material for supplying engine fuel. The Billings Energy Corporation is now testing a storage vessel rated at 25 kg of hydrogen at their Hydrogen Homestead.

At Argonne National Laboratory, a solar-driven heat pump based on cycling selected pairs of hydrides is being developed; it is presently planned to provide residential heating and cooling.

Use of a hydride's pressure characteristics is being applied in a hydride-hydrogen compressor under development at Ergenics, Inc., a division of MPD Technology Corp., and the Denver Research Institute (EDRI); and BNL is evaluating the use of a similar compressor as a head-end step in the liquefaction of hydrogen. Both compressors utilize waste heat and can thus provide substantial energy savings.