102
12-15-77
BNL 50714

MASTER

LB. 1670

ELECTROLYSIS BASED HYDROGEN STORAGE SYSTEMS

ANNUAL REPORT
JANUARY 1, 1976 TO DECEMBER 31, 1976

JANUARY 1977

Work Supported by the
DIVISION OF ENERGY STORAGE SYSTEMS
OFFICE OF CONSERVATION
UNITED STATES DEPARTMENT OF ENERGY

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

UNDER CONTRACT NO. EY-76-C-02-0016 WITH THE

UNITED STATES DEPARTMENT OF ENERGY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ELECTROLYSIS BASED HYDROGEN STORAGE SYSTEMS

**ANNUAL REPORT
JANUARY 1, 1976 TO DECEMBER 31, 1976**

F.J. SALZANO, Project Manager

Contributors:

A. Beaufriere	S. Majeski
M. Bonner	J. Milau
C. Braun	J. Reilly
K. Hoffman	M. Rosso
R. Isler	S. Srinivasan
J. Johnson	G. Strickland
G. Kissel	R. Wiswall
P. Lu	R. Yeo
	W. Yu

JANUARY 1977

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

**BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973**

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy (DOE), nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$7.25; Microfiche \$3.00

November 1977

350 copies

ELECTROLYSIS BASED HYDROGEN STORAGE SYSTEMS

Annual Report

January 1, 1976 to December 31, 1976

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.....	xi
FOREWORD.....	xiii
INTRODUCTION.....	xv
PUBLICATIONS.....	xvii
PAST PROGRESS REPORTS.....	xix
PROGRESS IN SCHEDULED AREAS	
AREA 1: ELECTROLYTIC HYDROGEN PRODUCTION	
1.1 Research on and Development of Advanced- Alkaline Water-Electrolysis Cells Operating at Temperatures between 120° and 150°C.....	1
1.2 Investigations on the BNL Two-Cell Model Bipolar Alkaline Water Electrolyzer Powered by Silicon Solar Cells.....	3
1.3 Nickel-Based Alloys as Electrocatalysts for the Oxygen Evolution Reaction from Alkaline Solutions.....	3
1.4 Mixed Oxides as Oxygen Electrodes.....	5
1.5 Correlations of Optical Properties and Thickness of Anodic Oxide Films with Their Electrocatalytic Activities for the O ₂ Evolution Reaction.....	7
1.6 Studies on a Reversible H ₂ -Cl ₂ Electro- chemical Cell.....	9

TABLE OF CONTENTS (continued)

	<u>Page</u>
Table 1.1 Electrode Kinetic Parameters for Oxygen Evolution Reaction on Ni, Ir and Some Nickel-Based Alloys from 30 Wt % KOH at 80°C...	12
1.2 Formation of Anodic Oxide Films on Ni, Ir and Pt Electrodes in the Oxygen Evolution Reaction at 25°C.....	13
Figure 1.1 Components of a single cell for evaluation of separator material and for half-cell measurements in alkaline water electrolysis at temperatures up to 160°C. Items 1 and 5 are dynamic hydrogen electrodes, 2 and 4 are test electrodes and 3 is separator material.....	14
1.2 Cell potential current-density relations for water electrolysis from 35% KOH with nickel elec- trodes and potassium titanate separator.....	15
1.3 Cyclic voltammograms for freshly- polished Ni, Ir and three Ni-Ir alloys in N ₂ -saturated 30 wt. % KOH solution at 80°C with a poten- tial sweep rate of 20 mV/sec.. Prior to the potential sweep, each electrode was maintained at -0.05 V vs. RHE for 20 minutes. The solid and dashed lines represent the first and second sweeps, respec- tively.....	16
1.4 Cathodic current density potential curves obtained from the repeating cyclic voltammograms on Ni, the intermetallic compound Ni ₃ Ti and the alloys of 50Ni-50Ir and 75Ni- 25Ru (atomic %) in O ₂ -saturated 30 wt % KOH solution at 80°C at a sweep rate of 20 mV/sec. Each	

TABLE OF CONTENTS (continued)

	<u>Page</u>
electrode was preanodized at a constant current density of 20 mA/cm ² for about 80 hours.....	17
1.5 Potential vs. current density curves for NiCo ₂ O ₄ prepared by freeze-drying method and used as Teflon-bonded electrodes. Curves represent steady-state, IR-corrected values at 22° and 80°C in 30% KOH.....	18
1.6 A ψ vs. Δ plot for a complete cycle of formation and reduction of α and β oxide films formed on Pt electrode after long-term polarization at 2.20 V in 1N H ₂ SO ₄ at 23°C.....	19
1.7 (A) Variation of the normalized differential reflectance with the electrode potential at $\theta = 65^\circ$ and $\lambda_0 = 5461 \text{ \AA}$. $(\delta R/R)_p$ and $(\delta R/R)_s$ are the normalized differential reflectance of the light polarized parallel (p) and perpendicular (s) to the plane of incidence. (B) Cyclic voltammogram for a freshly-polished Ni electrode in N ₂ -saturated 1N KOH with a linear sweep rate of 5 mV/sec.....	20
1.8 Variation of the ellipsometric parameters (Δ, ψ) with the electrode potential ($\theta = 65^\circ$ and $\lambda_0 = 5461 \text{ \AA}$). The steady-state measurements of Δ and ψ were carried out on a freshly-polished nickel electrode in 1N KOH at 25°C.....	21
1.9 Potential vs. current-density relations for H ₂ and Cl ₂ electrode reactions on smooth Pt by steady-state (x) and pulse-transient (o) techniques.....	22

TABLE OF CONTENTS (continued)

	<u>Page</u>
1.10 Cell potential vs. current-density relations for HCl electrolysis and the H_2-Cl_2 fuel cell reaction on a Pt-black ² screen with Nafion-115 as the separator material in 1.0 N HCl at 25°C (BNL Cell).....	23
1.11 Dependence of electrolyte flow rate on current density in the GE H_2-Cl_2 fuel cell at 25°C.....	24
1.12 Dependence of chlorine pressure on current density in the GE H_2-Cl_2 fuel cell at 25°C with 37% HCl ² as electrolyte.....	25
1.13 GE H_2-Cl_2 battery performance (Oct. 1976).....	26
References - Area 1.....	27

AREA 2: HYDROGEN STORAGE SUBSYSTEMS

2.1 Reference Designs and Process Systems...	31
2.2 Hydrogen Technology, Advanced-Component Test System (HYTACTS).....	33
2.3 Engineering Test Beds.....	34
2.4 Metal-Hydride-Material Test Beds.....	38
2.5 Container Materials Selection.....	41
2.6 Pressure Drop in Packed Beds.....	43
Table 2.1 Summary of ESEERCO Test Bed Data for Sustained-Flow-Rate Runs.....	47
2.2 Test Matrix for Self-Loaded Tensile Specimens Exposed to $FeTiH_x$	48

TABLE OF CONTENTS (continued)

	<u>Page</u>
Figure 2.1 Burns and Roe prototype module design.....	49
2.2 H ₂ -Cl ₂ Electrochemical Energy Storage Power Plant Schematic.....	50
2.3 HYTACTS flow diagram for the hydrogen storage section.....	51
2.4 Sketch of ESEERCO Test Bed.....	52
2.5 View of ESEERCO Test Bed operating area.....	53
2.6 ESEERCO Test Bed performance during hydriding.....	54
2.7 ESEERCO Test Bed performance during dehydriding.....	55
2.8 Pressure drop vs. hydrogen flow rate through a fixed bed.....	56
2.9 Pressure drop vs. particle size for hydrogen flow through a fixed bed.	57
References - Area 2.....	58
 AREA 3: HYDRIDE MATERIALS DEVELOPMENT	
3.1 Pressure-Composition Relationships.....	59
3.2 High-Cycle Testing.....	61
3.3 International Nickel Corp. Subcontract, "The Interrelations Among Composition, Microstructure and Hydriding Behavior for Alloys Based on the Intermetallic Compound FeTi".....	62
Table 3.1 Minimum-Temperature Activation Experiments.....	65
3.2 High-Cycle Test of Three Hydrides.	66

TABLE OF CONTENTS (continued)

	<u>Page</u>
3.3 Particle Size Distribution for TiFe _{0.7} Mn _{0.18} (INCO-1) and FeTi (NL-2) as a Function of Hydriding- Dehydriding Cycles.....	67
Figure 3.1 Pressure-composition desorption isotherms for the TiFe _{0.7} Mn _{0.2} -H system at several temperatures....	68
3.2 Hysteresis in the TiFe _{0.7} Mn _{0.2} -H system at 30°C.....	69
3.3 Pressure-composition desorption isotherms for the TiFe _{0.762} Mn _{0.136} - H system at several tempera- tures.....	70
3.4 Pressure-composition desorption isotherms for the TiFe _{0.762} Mn _{0.138} - H system at several tempera- tures.....	71
3.5 Hysteresis in the TiFe _{0.762} Mn _{0.136} - H system at 40°C.....	72
3.6 Hysteresis in the TiFe _{0.762} Mn _{0.138} - H system at 40°C.....	73
3.7 Pressure-composition desorption isotherms for the TiFe _{0.79} Mn _{0.15} -H system (INCO-2) at 40°C.....	74
3.8 A comparison of pressure-composi- tion desorption isotherms for alloys of similar composition at 40°C....	75
3.9 Pressure-composition desorption isotherms for the FeTi-H system (INCO-3) at 40°C.....	76
3.10 Pressure-composition desorption isotherms for the TiFe _{0.9} Mn _{0.1} -H system at 85°C.....	77
3.11 High-cycle test showing effect of 1.1 mol % O ₂ in hydrogen. The amplitude of the right-hand trace	

TABLE OF CONTENTS (continued)

	<u>Page</u>
is proportional to the activity of FeTi to hydrogen.....	78
3.12 High-cycle test showing effect of 0.10 mol % O ₂ in hydrogen. The amplitude of the right-hand trace is proportional to the activity of FeTi to hydrogen.....	79
3.13 High-cycle test showing effect of 0.011 mol % O ₂ in hydrogen. The amplitude of the right-hand trace is proportional to the activity of FeTi to hydrogen.....	80
3.14 High-cycle test showing effect of 0.001 mol % O ₂ in hydrogen. The amplitude of the right-hand trace is proportional to the activity of FeTi to hydrogen.....	81
 AREA 4: NATURAL GAS SUPPLEMENTATION.....	 83
 AREA 5: HYDROGEN STORAGE SYSTEMS ANALYSIS	
5.1 Studies and Assessments.....	85
Table 5.1 Computation of Hydrogen Production Costs by Various Technologies in the Years 1985 and 2000.....	91
Footnotes for Table 5.1.....	92
References - Area 5.....	94
 AREA 6: PROJECT MANAGEMENT	
6.1 Planning and Analysis.....	97
6.2 Contract Management.....	98
6.3 Technical Management.....	99

TABLE OF CONTENTS (continued)

	<u>Page</u>
6.4 Liaison Activities.....	99
References - Area 6.....	101
APPENDIX A.....	103
Figure 3A1 Pressure-composition desorption isotherms for the $\text{TiFe}_{0.6}\text{Mn}_{0.2}\text{-H}$ system at several temperatures.....	104
3A2 Hysteresis in the $\text{TiFe}_{0.6}\text{Mn}_{0.2}\text{-H}$ system at 30°C.....	105
3A3 Pressure-composition desorption isotherms for the $\text{TiFe}_{0.6}\text{Mn}_{0.3}\text{-H}$ system at several temperatures.....	106
3A4 Hysteresis in the $\text{TiFe}_{0.6}\text{Mn}_{0.3}\text{-H}$ system at 30°C.....	107
3A5 Pressure-composition desorption isotherms for the $\text{TiFe}_{0.5}\text{Mn}_{0.3}\text{-H}$ system at several temperatures.....	108
3A6 Hysteresis in the $\text{TiFe}_{0.5}\text{Mn}_{0.3}\text{-H}$ system at 30°C.....	109
3A7 Pressure-composition desorption isotherms for the $\text{TiFe}_{0.5}\text{Mn}_{0.2}\text{-H}$ system at several temperatures.....	110
3A8 Pressure-composition desorption isotherms for the $\text{TiFe}_{0.7}\text{Mn}_{0.18}\text{-H}$ system (INCO-1) at several temperatures.....	111
3A9 Hysteresis in the $\text{TiFe}_{0.7}\text{Mn}_{0.18}\text{-H}$ system (INCO-1) at 30°C.....	112

ABSTRACT

This report describes work completed during the period January 1, 1976 to December 31, 1976, on an ERDA sponsored program aimed at improvement in the cost and efficiency of electrolytic hydrogen production and development of the technique of using metal hydrides for hydrogen storage for stationary and transportation applications. The work on electrolytic hydrogen production includes work on advanced barrier materials for alkaline cells, studies of nickel alloy based and oxide catalysts for oxygen evolution. Related work on the program involving the H_2-Cl_2 electrochemical cell for energy storage is described. Work on hydrogen storage subsystems involving storage reservoir designs for the Hydrogen Technology Advanced-Component Test System (HYTACTS), engineering and metal hydride material test beds and tests of candidate container materials is presented. Progress on the development of new metal hydride materials and tailoring and testing of new alloy systems is summarized. This work emphasizes improvement in the initial activation step, high-cycle test of selected materials and the physical characteristics of cycled materials. The effort on natural gas supplementation, hydrogen storage systems analysis and the project management of the ERDA Hydrogen Program by BNL are summarized.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

FOREWORD

This report describes a program supported by the U.S. Energy Research and Development Administration, Division of Energy Storage, for the development of the technology of electrolytic hydrogen production, storage, and reconversion to electricity. The emphasis is on the improvement in the cost and efficiency of electrolytic hydrogen production and the use of metal hydrides for hydrogen storage. The program involves major efforts by industrial subcontractors and work carried out by staff at BNL.

The scientific basis for the use of metal hydrides for hydrogen storage was established in a program at the Brookhaven National Laboratory under way since 1967 and now supported by the Energy Research and Development Administration, Division of Basic Energy Sciences. The primary goal of this program is the development of the technology, hardware, and technical skills required in the application of hydrogen as an energy storage medium, and in the general application of hydrogen in selected sectors of the U.S. energy system. An application of hydrogen storage is the use in an electric-to-electric energy storage scheme involving the electrolysis of hydrochloric acid. Design work on a full-scale storage plant has been initiated along with systems analysis studies of energy storage in utility systems.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

INTRODUCTION

This program is concerned with the further development of the technique of electrolytic hydrogen production and storage for use in various energy storage applications. The Energy Research and Development Administration, Division of Energy Storage, Chemical and Thermal Branch, is supporting this program which has the goal of developing the technology, hardware and technical expertise necessary to improve the efficiency and reduce the cost of electrolytic hydrogen production. A second goal of the program is to develop the technique of using metal hydrides for hydrogen storage in a range of applications which include stationary and transportation uses and applications in the chemical industry.

An important emphasis of the program is the application of hydrogen storage in an electric-to-electric storage scheme based on the electrolysis of hydrochloric acid to hydrogen and chlorine, which are stored, and subsequent reconversion in the same electrochemical cell to electric energy. This concept appears to be a very promising and flexible alternative for pumped storage and peaking gas turbines, which are limited by lack of suitable sites and the inefficient use of high grade fuels, respectively, as well as for storage of solar energy.

In the work on hydrogen storage, the emphasis is on the application of metal hydrides, other hydrogen storage options, high-pressure gas and liquid hydrogen are given due consideration. The program recognizes that the development of a low-cost efficient method of hydrogen production is essential if nuclear and solar energy or other renewable resources are to be used to supply some of the fuel needs of the future, presently supplied by natural gas and petroleum.

The program is organized into four major areas:

Area 1: Electrolytic Hydrogen Production

Area 2: Hydrogen Storage Subsystems

Area 3: Hydride Materials Development

Area 4: Natural Gas Supplementation

The program activities associated with these four areas involve a range of activities in which a major fraction of funds and effort is carried out by industry with the remaining activities centered at BNL. A scope of work is given at the beginning of each area of the progress report.

PUBLICATIONS

J. J. Reilly, J. Johnson, Titanium Alloy Hydrides, Their Properties and Applications, Informal Report, December 1975. (BNL 20791)

G. Strickland, J. Milau, W-S Yu, The behavior of iron titanium hydride test beds: long-term effects, heat transfer and modeling, presented at the 1st World Hydrogen Energy Conference, Miami, Florida, March 1-3, 1976. (BNL 20876)

F. J. Salzano, C. Braun, A. H. Beaufrere, S. Srinivasan, G. Strickland, J. Reilly, Hydrogen for energy storage: a progress report of technical developments and possible applications, presented at the Engineering Foundation Energy Storage Conference, Pacific Grove, California, February 8-13, 1976. (BNL 20931)

S. Srinivasan, Hydrogen production by water electrolysis: present status and future prospects, presented at Electrochemistry Meeting, Zurich, Switzerland, September 6-11, 1976. (BNL 21481)

F. J. Salzano, C. Braun, A. Beaufrere, S. Srinivasan, G. Strickland, J. Reilly, Hydrogen storage water electrolysis and fuel cells for electric energy storage, presented at the Energy Conference, Grenoble, France, April 9, 1976. (BNL 21498)

J. Reilly, G. Sandrock, J. Johnson, Metallurgical considerations in the production and use of FeTi alloys for hydrogen storage, presented at the 11th Intersociety Energy Conversion and Engineering Conference, State Line, Nevada, September 1976. (BNL 21539)

F. J. Salzano, S. Srinivasan, Solid electrolyte and elevated temperature water electrolysis, presented at the AIM Meeting, Liege, Belgium, November 15-18, 1976. (BNL 21547)

F. J. Salzano, C. Braun, A. Beaufrere, S. Srinivasan, G. Strickland, J. Reilly, C. Waide, Hydrogen storage via metal hydrides for utility and automotive energy storage applications, presented at the 26th Canadian Society of Chemical Engineers, Toronto, Canada, October 4-6, 1976. (BNL 21723)

F. J. Salzano, E. Gileadi, S. Srinivasan, C. Braun, A. Beaufrere, S. Gottesfeld, An electrochemically regenerative hydrogen-chlorine energy storage system for electric utilities, presented at the 11th Intersociety Energy Conversion and Engineering Conference, State Line, Nevada, September 1976. (BNL 21820)

M. J. Rosso, G. Strickland, J. Milau, Pressure-Drop-Fluid
Flow Correlation for Fixed Beds of Small, Irregularly Shaped
Particles, November 1976. (BNL 50589)

PAST PROGRESS REPORTS

F. J. Salzano, Editor. Hydrogen Storage and Production in Utility Systems, First Quarterly Progress Report, November 1 to December 31, 1973. BNL 18603. January 1974.

F. J. Salzano, Editor. Hydrogen Storage and Production in Utility Systems, Second Quarterly Progress Report, January 1 to March 31, 1974. BNL 18920. April 1974.

F. J. Salzano, Editor. Hydrogen Storage and Production in Utility Systems, First Annual Report, November 1, 1973 to June 30, 1974. BNL 19249. July 1974.

F. J. Salzano, Editor. Hydrogen Storage and Production in Utility Systems, Third Quarterly Progress Report, July 1 to September 30, 1974. BNL 19520. October 1974.

F. J. Salzano, Editor. Hydrogen Storage and Production in Utility Systems, Fourth Quarterly Progress Report, October 1 to December 31, 1974. BNL 20040. January 1975.

F. J. Salzano, Editor. Hydrogen Storage and Production in Utility Systems, Fifth Quarterly Progress Report, January 1 to March 31, 1975. BNL 20420. April 1975.

F. J. Salzano, Editor. Hydrogen Storage and Production in Utility Systems, Second Annual Progress Report, July 1, 1974 to June 30, 1975. BNL 50472. August 1975.

F. J. Salzano, Project Manager. Hydrogen Production and Storage in Utility Systems, Semiannual Progress Report, July 1, 1975 to December 31, 1975. BNL 50590. January 1976.

AREA 1: ELECTROLYTIC HYDROGEN PRODUCTION

Scope:

Examine the chemistry, physics, and materials problems associated with advanced electrolytic concepts including low- and intermediate-temperature aqueous, high-temperature fused salt, and solid-electrolyte systems. This activity involves a review of the past development efforts of other investigators in light of recent developments and improvements in materials. The emphasis will be on the development of high performance systems, the ultimate goal being electric-to-hydrogen conversion efficiencies exceeding 90% (thermal efficiency) and installed capital costs below \$50/kW thermal hydrogen output. An effort will be made to continuously review progress in the development of other production methods, e.g., thermochemical and biological.

1.1 Research on and Development of Advanced-Alkaline Water-Electrolysis Cells Operating at Temperatures Between 120° and 150°C

One of the biggest problems in developing alkaline water electrolysis cells operating at temperatures between 120° and 150°C is to find stable barrier and other structural materials. Thus, the main effort for the reporting period was on the selection and evaluation of these materials [1,2,3]. All of the anionic membranes tested were unsatisfactory. They exhibited relatively high resistance and, in most cases, poor thermal stability in alkaline electrolytes. Cationic membranes perform satisfactorily in alkaline cells. They tend to "dehydrate" at elevated temperatures in 30 wt % alkali. However, it is possible to trade off some increase in electrolyte resistance for a decrease in membrane resistance by lowering the hydroxyl-ion concentration. Cationic membranes also have a lower resistance in sodium hydroxide compared with potassium hydroxide at the same ionic concentration. At the present time, the following

barrier materials appear to be suitable for long term, higher temperature water electrolysis ($120^{\circ} - 150^{\circ}\text{C}$): (1) Nafion (cationic membrane); (2) potassium titanate (fibrous material); and (3) RAI 1010 membrane (cationic membrane). Boron nitride, which appeared satisfactory at temperatures less than 100°C , disintegrated in the strong alkaline environment at higher temperatures.

For higher temperature water electrolyzers, potential candidates for cell construction materials are polysulfone for temperatures of $120^{\circ} - 150^{\circ}\text{C}$, and Teflon-based materials for temperatures over 150°C . The main problem, encountered to date in the construction of small test cells, has been obtaining gasket materials which are stable in the alkaline environment at the elevated temperatures. Viton gaskets are unstable, whereas ethylene-propylene gaskets are resistant to chemicals and heat, but are rather poor sealants. At high temperatures, Teflon-encapsulated, silicone rubber gaskets may be required. The changes in cathode and anode potentials show that the cathode is much more sensitive to poisoning by decomposition products.

The test cell design in present use consists of a 4-unit plastic assembly held together by two stainless steel end plates with appropriate bolts, nuts and springs (Figure 1.1). A tension device (not shown) is used to maintain the gasket seal during temperature changes. The working electrodes are wire-mesh Ni and the reference electrodes are dynamic H_2 electrodes maintained at 1 mA/cm^2 . In operation, the electrolyte level is maintained by controlled purging with the stream which is used to remove accumulated H_2 and O_2 gases from the pressure vessel. The cell potential vs. current-density relations for alkaline water electrolysis, with potassium titanate as the separator material, are shown for several operating temperatures in Figure 1.2. At the present time, it is recommended that an

operating temperature of 120°C be chosen for advanced-alkaline, water-electrolysis cell development. As seen from Figure 1.2, there is a considerable improvement in cell performance when the operating temperature is increased from 97° to 130°C, whereas the increase is less when the temperature is further elevated to 150°C. There is a considerably better prospect of finding cell construction materials which are stable at 120°C than at 150°C in the strong alkaline environment.

Advanced cell configurations, mixed electrolytes and modified electrode materials and designs are under study.

1.2 Investigations on the BNL Two-Cell Model Bipolar Alkaline Water Electrolyzer Powered by Silicon Solar Cells

Some operating experience was obtained on a small H₂ production system using a silicon solar-cell array coupled to a BNL-built bipolar electrolyzer operating at room temperature with 20% NaOH as the electrolyte. No other source of power is required, and only DC power is involved. In one cell the gas barrier material is Nafion 115 and in the other it is RAI 1010; both are cationic-exchange membranes. The only maintenance required over the six months of operation was cleaning of the plastic cover for the cell array, monthly angle adjustment of the array, and addition of make-up water to the electrolyzer. A recording of the power output showed that the maximum level was ~8 watts, with the average being 3-4 watts. The array was temperature sensitive, with the result that on a cooler, cloudy day the output was comparable with that on a warmer, sunny day. The test was concluded at the end of November when the level of radiant energy became low.

1.3 Nickel-Based Alloys as Electrocatalysts for the Oxygen Evolution Reaction from Alkaline Solutions

In the Teledyne water electrolysis cells, Ni is used as the electrocatalyst for the O₂ evolution reaction. The slowness of this reaction is the major cause of efficiency loss in water electrolysis cells [4]. It has been reported [5]

that the electrocatalytic properties of an alloy may parallel the changes in its electronic properties, such as d-band vacancies. By alloying Ni with other transition metals containing more unpaired d-electrons, one may expect an increase in the number of d-band vacancies and, consequently, an enhancement in the electrocatalytic activity. On the basis of this prediction, three intermetallic compounds: Ni_3Ti , NiTi , NiTi_2 ; and alloys of Ni with Ir, Ru or W (composition: 25, 50 and 75 atomic % Ni) were investigated as O_2 electrodes in 30 wt % KOH at 80°C [6,7].

The Tafel plots for the O_2 evolution reaction on mechanically-polished electrodes of these alloys and intermetallic compounds, and on Ni and Ir, were determined using steady-state potentiostatic and slow-potentiodynamic (0.1 mV/sec) methods. The electrode kinetic parameters for O_2 evolution are summarized in Table 1.1. Most of the stable alloys or intermetallic compounds in Ni-Ir, Ni-Ru and Ni-Ti systems exhibit Tafel slopes and exchange-current densities similar to those of Ni. With the Ni-W alloys and the metallic compound NiTi_2 , on which poorly conducting oxide films are formed, abnormally high Tafel slopes and exchange-current densities were observed. These unusually high Tafel slopes were successfully interpreted by means of the dual barrier layer of Meyer [8]. The decrease in O_2 overpotential (η) for the alloys 50Ni-50Ir and 75Ni-25Ru and the intermetallic compound Ni_3Ti were 40, 30 and 20 mV, respectively, compared with that for Ni at a current density of 20 mA/cm^2 .

Because the O_2 evolution reaction always takes place on an oxide-covered surface, the nature of the mixed-oxide films formed on these alloys was studied in N_2 -saturated 30 wt % KOH (to eliminate O_2 interference) at 80°C using cyclic voltammetric techniques. As shown in Figure 1.3, the peaks for the formation or reduction of O_2 -containing layers appearing on the pure Ni and Ir are not always found on the alloys. Obviously, the electro-

chemical activities of the individual components in the alloys play a significant role in the reaction of oxide formation on the electrode surface of these alloys.

After anodization in O_2 -saturated, 30 wt % KOH at a constant current of 20 mA/cm^2 for 80 hours, the O_2 -containing layers on Ni, on the alloys 50Ni-50Ir and 75Ni-25Ru, and on the intermetallic compound Ni_3Ti were characterized using cyclic voltammetric techniques. The first, second and tenth traces of the cathodic i-V curves for these electrode materials are shown in Figure 1.4. For the alloys of 50Ni-50Ir and 75Ni-25Ru, the first i-V curves are essentially similar to the curve for Ni. No distinguishable reduction peaks are observed, except for the ones corresponding to the reduction of $\beta\text{-NiOOH}$. These observations indicate that the O_2 -containing layers of these alloys are substantially composed of Ni oxides instead of true mixed-oxide films of two components. This behavior probably explains why the kinetic parameters for the O_2 evolution reactions on the Ni-Ir or Ni-Ru alloys are so similar to those on Ni.

1.4 Mixed Oxides as Oxygen Electrodes

A major cause of inefficiency in water electrolysis cells, some fuel cells, and metal-air batteries is the irreversibility of the O_2 electrode reaction. Oxygen evolution always occurs on oxide-covered surfaces, whereas O_2 reduction can occur either on bare metal surfaces or on oxides; thus, metal oxides are the only promising candidates for reversible O_2 electrodes [9, 10]. In particular, spinels [11] and perovskites [12] have shown potential for high electrocatalytic activity.

Conventional methods of preparing oxides involve solid-state reactions at elevated temperatures; however, the resultant products generally have very low surface areas and correspondingly low apparent activity. Therefore, a freeze drying technique [13], described below, was employed to prepare a wide range of oxides for examination. Solutions of the corresponding nitrates were

sprayed into a tray of liquid nitrogen; this procedure eliminates segregation of the salts (due to varying solubilities) and results in an atomically dispersed solid solution. The solid solution was then vacuum dried while being maintained at a temperature below its triple point in order to prevent melting and possible segregation. The mixed nitrates were then decomposed, in vacuum, to the oxide. Low-temperature calcining in air follows, yielding the stoichiometric oxide in the form of a high-surface-area powder.

It is well known that electrocatalytic activity is dependent on electronic factors (e.g., density and energy levels of surface states). It has also been proposed that activity toward O_2 reduction may depend on magnetic properties [14]. A paramagnetic material will promote "side-on" adsorption of the O_2 molecule resulting in an increased performance. Oxides are now being prepared and evaluated on this basis. Electrochemical studies were performed with a PAR 173 potentiostat and a PAR 175 voltage programmer. Both steady-state and transient techniques were employed at temperatures ranging to $80^\circ C$ in evaluating electrocatalytic activity. Long-term stability will be determined under test conditions with concurrent corrosion evaluation.

Early reports [15] of the good catalytic properties of the spinel $NiCo_2O_4$ have prompted its preparation and evaluation. The oxide, prepared via the method outlined above, resulted in a powder having a surface area of $41\text{ m}^2/\text{g}$, as determined by a dynamic BET method. The oxides were evaluated as Teflon-bonded electrodes in which the oxide was mixed in a ratio of 10:3 by weight with Teflon (polytetrafluoroethylene) in a water dispersion. The catalyst mixture was painted on a Ni screen and heat treated at $300^\circ C$ for one hour. The polarization curves for O_2 evolution on $NiCo_2O_4$ in 30 wt % KOH at 22° and $80^\circ C$ are shown in Figure 1.5. The results indicate an

improved performance with respect to decreased time variation of cell potential for H_2O electrolysis. Studies are presently underway to evaluate long-term performance and stability of NiCo_2O_4 in test electrolyzers. In addition, a cooperative test program has been initiated with Teledyne Energy Systems in order to facilitate transfer of technology to industry.

1.5 Correlations of Optical Properties and Thickness of Anodic Oxide Films with Their Electrocatalytic Activities for the O_2 Evolution Reaction

The O_2 evolution reaction occurs only on oxide films formed on an electrode surface during the anodic polarization. One can expect the kinetics of this reaction to depend on the properties of these films: namely, electronic conductivity, thickness and chemical composition. The Teledyne water electrolyzers use Ni as the O_2 electrode material, whereas the General Electric SPE water electrolysis cells use an Ir-based alloy as the electrocatalyst for O_2 evolution. As has been pointed out [4], the low electrocatalytic activity of these oxide films can be one of the major sources of efficiency losses in water electrolyzers. Ellipsometry and reflectometry, which allow nondestructive measurements in situ of the thickness and optical constants of thin films, were employed to characterize the anodic oxide layer formed on Pt, Ir and Ni. As described below, a further effort was made to correlate the optical constants of oxide films with their electrocatalytic activities for O_2 evolution.

After polarization of a Pt electrode, at 2.20V vs. RHE for 140 minutes in 1N H_2SO_4 , two different types of oxide films, designated as α and β , were present on the electrode surface. As shown in Figure 1.6, these two films are readily distinguished by the opposite effects they have on the ellipsometric parameter of amplitude attenuation, ψ , which decreases with growth of the α film thickness and increases with growth of the β film thickness. The α film inhibits O_2 evolution on Pt. The dependence

of the current density for O_2 evolution on the thickness of the film, d_α , is given by [16]:

$$i = A \exp (-Bd_\alpha) \exp (FE/2RT), \quad (1.1)$$

where A and B are constants and F is the Faraday.

The β film, which grows on top of the α film due to anodic breakdown of the latter film, was a highly hydrated and porous form of oxide film. Ellipsometric results indicated that the β film, having a very low value of κ (the absorption coefficient, ~ 0.01), is a poor electronic conductor. However, this film is a better electrocatalyst for O_2 evolution. Formation of the β film caused a significant decrease of the observed Tafel slope, from ~ 115 to ~ 80 mV.

Characterization of the anodic oxide layer formed on Ni in the low potential range for the oxide formation was carried out in 1N KOH. As shown in Figure 1.7 and Figure 1.8, the formation of the highly absorbing species, β -NiOOH, results in not only considerable decreases in the normalized differential reflectance (more than 60%), but also significant changes in the ellipsometric parameters of relative phase retardation, Δ , and amplitude attenuation, ψ . These observations indicate that the species β -NiOOH has properties similar to those of a good electronic conductor.

Ellipsometric and reflectometric studies were also conducted on Ni and Ir electrodes in 1N KOH and on an Ir electrode in 1M H_2SO_4 after the electrodes were polarized at potentials in the O_2 evolution region. The results are summarized in Table 1.2. The anodic oxide film formed on Ni electrodes was confirmed to be a non-stoichiometric oxide layer, consisting mainly of Ni^{3+} and Ni^{4+} ions. The electrical resistance of this film increased with the polarization time, as indicated by the increasing thickness of the film and by the slight decrease of its conductivity.

After anodization in alkaline solutions, oxide films on polarized Ni or Ir electrode surfaces exhibited high values of absorption coefficients, and thus are good electronic conductors. In acid media, the oxide films formed on Ir electrodes tended to dissolve anodically at the potential of 2.2V. Conversely, poorly conducting oxide films have been observed on Pt electrodes [17]. These results probably explain why the measured exchange current densities for the O_2 evolution reaction on Ni or Ir oxide films are remarkably higher than for this reaction on Pt oxide films, by a factor of about 10^3 to 10^4 . The results of the present work show that the electronic conductivity of oxide films plays a significant role in the determination of the electrocatalytic activities of electrode materials for the O_2 evolution reaction.

1.6 Studies on a Reversible H_2 - Cl_2 Electrochemical Cell

Experimental work was initiated on a H_2 - Cl_2 electrochemical cell because its reversible behavior makes it superior to the H_2 - O_2 cell. The H_2 - Cl_2 system was proposed for use as an electric storage battery by Bianchi in 1964 [18, 19], and as a power recovery system for and as a power recovery system for caustic-chlorine plants [20]. Recently this system was proposed [21] for energy storage applications for electric utility companies. In the charging mode HCl is electrolyzed with off-peak power, producing H_2 and Cl_2 , and in the discharging mode these reactants combine to produce electrical power. Because the electrochemical reactions are reversible, the unit can be expected to function as an electrolyzer and as a fuel cell, using the same electrocatalysts, with an electric-to-electric efficiency of over 75%. Information on other aspects of the H_2 - Cl_2 system is given in Section 2.1 of this report.

Steady state electrocatalysis investigations of H_2 and Cl_2 half-cell reactions have shown that Pt is a better catalyst than the widely used graphite [19, 22, 23, 24, 25]. Cyclic voltammetry techniques were also employed in studying these reactions.

Studies of the Cl_2 electrode reaction showed that $\text{RuO}_2/\text{TiO}_2$ is also a promising catalyst.

In the studies made at BNL, the H_2 and Cl_2 half-cell reactions on smooth Pt were examined by two techniques. In the steady-state method the reaction rates were limited by mass transfer of the reactants to the electrode surface; but in the pulse-transient method there was improved performance, and as shown in Figure 1.9, higher current densities were obtained.

A cell was designed and fabricated for determining its performance in both the HCl -electrolysis and the H_2 - Cl_2 fuel-cell modes. The interelectrode spacing was minimal and Nafion 115 was used as the separator. As shown in Figure 1.10 the activation overpotential is quite small, indicating that a high electric-to-electric efficiency can be expected for this electrochemically regenerative cell.

A solid-polymer-electrolyte (SPE) cell, designed and fabricated by General Electric Company, was evaluated in both the HCl -electrolysis (charge) mode and the H_2 - Cl_2 fuel cell (discharge) mode. The voltage vs. current-density relationships obtained resembled those shown in Figure 1.10 for the BNL cell. In the discharge mode the current density is highly diffusion controlled under normal conditions, but this limitation can be overcome by increasing the flow rate of the electrolyte at the Cl_2 electrode. Figure 1.11 shows the great improvement made in this manner. The cell potential is lowered and the current density is increased as the flow rate is increased. Further improvement was sought by increasing the Cl_2 pressure in order to increase its solubility in the electrolyte. Using a pressure vessel constructed for this purpose, the results shown in Figure 1.12 were obtained. Thus similar improvements were realized as a function of increasing cell pressure. Although both cells performed well in the electrolysis mode, performance in the fuel cell mode was poor ($<10 \text{ ma/cm}^2$).

With the new Cl_2 electrode design, linear potential vs. current-density relations were obtained for both operating modes over the current-density range from 0 to 400 mA/cm^2 , as shown in Figure 1.13.

Table 1.1 Electrode Kinetic Parameters for Oxygen Evolution Reaction on Ni, Ir and Some Nickel-Based Alloys from 30 Wt % KOH at 80°C

Electrode	b (volt)		α		i_o (A/cm ²)		η_a at 20 mA/cm ² (volt)
	low η	high η	low η	high η	low η	high η	
Pure Ni	0.062		1.1		2.3×10^{-7}		0.31
75 Ni - 25 Ir*	0.067		1.0		8.8×10^{-7}		0.29
50 Ni - 50 Ir*	0.047	0.086	1.5	0.81	3.4×10^{-8}	2.0×10^{-5}	0.27
25 Ni - 75 Ir*	0.064		1.1		6.0×10^{-7}		0.29
Pure Ir	0.055		1.3		5.0×10^{-8}		0.32
75 Ni - 25 Ru*	0.056		1.3		2.4×10^{-8}		0.28
75 Ni - 25 W*	0.114		0.61		4.6×10^{-5}		0.30
50 Ni - 50 W*	0.125		0.56		2.5×10^{-4}		-- **
Ni ₃ Ti	0.064		1.1		4.7×10^{-7}		0.29
NiTi	0.057	0.094	1.3	0.74	6.0×10^{-8}	2.8×10^{-6}	0.35
NiTi ₂	0.333		0.13		6.5×10^{-5}		-- †

* In atomic %.

** The observed current densities in the Tafel region for the O₂ evolution reaction on 50 Ni - 50 W are above 40 mA/cm²

† Limiting current density of NiTi₂ is about 3 mA/cm²

Table 1.2 Formation of Anodic Oxide Films on Ni, Ir and Pt Electrodes in the Oxygen Evolution Reaction at 25°C

Electrode	Solution	¹ E (V/RHE)	² t (hrs.)	³ i _f (mA/cm ²)	⁴ i _o (A/cm ²)	Thickness (Å)	Refractive Index, n _f	Absorption Coef. k _f
Ni	1N KOH	2.0	3.4	15.2	3.1x10 ⁻⁶	~210	1.80	2.72
Ni	1N KOH	2.0	21.4	11.8	3.1x10 ⁻⁷	~410	1.45	2.48
Ir	1N KOH	2.0	2.0	25.0	3.9x10 ⁻⁸	~40	2.66	3.60
Ir	1N KOH	2.0	22.0	8.2	2.0x10 ⁻⁸	~90	2.06	2.84
Ir	1M H ₂ SO ₄	2.2	2.0	175.0	4.5x10 ⁻⁷	--	--	--
⁵ Pt	1M H ₂ SO ₄	2.2	2.3	--	3.3x10 ⁻¹¹	~85	2.10	0.00-0.02

1. E = Polarization potential

2. t = Polarization time

3. i_f = Final current density at the end of t

4. i_o = Exchange current density

5. Data from the work of Gottesfeld and Srinivasan⁽¹⁷⁾

Figure 1.1 Components of a single cell for evaluation of separator material and for half-cell measurements in alkaline water electrolysis at temperatures up to 160°C. Items 1 and 5 are dynamic hydrogen electrodes, 2 and 4 are test electrodes and 3 is separator material.

Figure 1.2 Cell potential current-density relations for water electrolysis from 35% KOH with nickel electrodes and potassium titanate separator.

Figure 1.3 Cyclic voltammograms for freshly-polished Ni, Ir and three Ni-Ir alloys in N_2 -saturated 30 wt. % KOH solution at 80°C with a potential sweep rate of 20 mV/sec. Prior to the potential sweep, each electrode was maintained at -0.05 V vs. RHE for 20 minutes. The solid and dashed lines represent the first and second sweeps, respectively.

Figure 1.4: Cathodic current density potential curves obtained from the repeating cyclic voltammograms on Ni, the intermetallic compound Ni₃Ti and the alloys of 50Ni-50Ir and 75Ni-25Ru (atomic %) in O₂-saturated 30 wt. % KOH solution at 80°C at a sweep rate of 20 mV/sec. Each electrode was preanodized at a constant current density of 20 mA/cm² for about 80 hours.

POLARIZATION CURVES FOR NiCo_2O_4

Figure 1.5 Potential vs. current density curves for NiCo_2O_4 prepared by freeze-drying method and used as Teflon-bonded electrodes. Curves represent steady-state, IR-corrected values at 22°C and 80°C in 30% KOH.

Figure 1.6 A ψ vs. Δ plot for a complete cycle of formation and reduction of α and β oxide films formed on a Pt electrode after long-term polarization at 2.20 V in 1N H_2SO_4 at 23°C.

Figure 1.7 (A) Variation of the normalized differential reflectance with the electrode potential at $\theta = 65^\circ$ and $\lambda = 5461 \text{ \AA}$. $(\delta R/R)_p$ and $(\delta R/R)_s$ are the normalized differential reflectance of the light polarized parallel (p) and perpendicular (s) to the plane of incidence. (B) Cyclic voltammogram for a freshly-polished Ni electrode in N_2 -saturated 1N KOH with a linear sweep rate of 5 mV/sec.

Figure 1.8 Variation of the ellipsometric parameters (Δ, ψ) with the electrode potential ($\theta = 65^\circ$ and $\lambda_0 = 5461\text{\AA}$). The steady-state measurements of Δ and ψ were carried out on a freshly-polished nickel electrode in 1N KOH at 25°C .

Figure 1.9 Potential vs. current-density relations for H₂ and Cl₂ electrode reactions on smooth Pt by steady state (x) and pulse-transient (o) techniques.

Figure 1.10 Cell potential vs. current-density relations for HCl electrolysis and the $\text{H}_2\text{-Cl}_2$ fuel cell reaction on a Pt-black screen with Nafion[®] 115₂ as the separator material in 1.0 N HCl at 25°C (BNL Cell).

Figure 1.11 Dependence of electrolyte flow rate on current density in the GE H₂-Cl₂ fuel cell at 25°C.

Figure 1.12 Dependence of chlorine pressure on current density in the GE H_2-Cl_2 fuel cell at 25°C with 37% HCl as electrolyte.

Figure 1.13 GE H₂-Cl₂ battery performance (Oct. 1976).

Area 1: Electrolytic Hydrogen Production

References

- [1] Hydrogen Storage and Production in Utility Systems, Semiannual Progress Report, July 1, 1975 to December 31, 1975, F. J. Salzano, Project Manager, BNL 50590, January 1976.
- [2] S. Srinivasan, F. J. Salzano, Prospects for hydrogen production by water electrolysis to be competitive with conventional methods, Proceedings of the First World Hydrogen Energy Conference, Volume II, pp. 6B-23-6B-37, Miami, Florida, March 1976.
- [3] S. Srinivasan, F. J. Salzano, Solid electrolyte and elevated temperature water electrolysis, Proceedings of the A.I.M. Meeting on Hydrogen and Its Prospects, Liege, Belgium, November 1976, in press.
- [4] M. W. Breiter, Advances in electrochemistry and electrochemical engineering, P. Delahay and C. W. Tobias, Editors, Interscience, Volume 1, Chap. 3, New York (1961).
- [5] E. W. Brooman, A. T. Kuhn, Correlations between the rates of the hydrogen electrode reaction and the properties of alloys, J. Electroanal. Chem., 49, 325 (1974).
- [6] P. W. T. Lu, S. Srinivasan, Nickel based alloys as electrocatalysts for oxygen evolution from alkaline solutions, 149th Meeting of the Electrochemical Society, Washington, D.C., May 1976 (BNL 22654).
- [7] P. W. T. Lu, Oxygen Electrodes: Electrochemical and Ellipsometric Studies, Ph.D. Thesis, SUNY at Stony Brook, Stony Brook, New York (1976).
- [8] R. E. Meyer, Cathodic processes on passive zirconium, J. Electrochem. Soc., 107, 847 (1960).
- [9] G. Singh, M. H. Miles, S. Srinivasan, Mixed oxides as oxygen electrodes, Proceedings of the Workshop in Electrocatalysis on Non-Metallic Surfaces, National Bureau of Standards, Gaithersburg, Maryland, pp. 289-296, 1975 (BNL 20984).
- [10] S. Trassatti, G. Buzzanca, Ruthenium Dioxide: A new interesting electrode material solid state structure and electrochemical behavior, J. Electroanal. Chem., 29, App.1 (1971).

- [11] R. A. Humphrey, Ph.D. dissertation, OSU (1955).
- [12] A. C. C. Tseung, H. L. Bevan, A reversible oxygen electrode, J. Electroanal. Chem., 45, 429 (1973).
- [13] A. C. C. Tseung, H. L. Bevan, Preparation and characterization of high surface area semiconducting oxides, J. of Mat. Sci., 604 (1970).
- [14] E. R. S. Winter, Adsorption upon pure and lithium doped nickel oxide, J. of Catalysis, 6, 35 (1966).
- [15] A. C. C. Tseung, Oxygen evolution on semiconducting oxides, Electrochim. Acta, 23, 31 (1977).
- [16] A. Damjanovic, A. T. Ward, M. O'jea, Effects of the thickness of anodic oxide films on the rate of the oxygen evolution reaction at Pt in H_2SO_4 solution, J. Electrochem. Soc., 121, 1186 (1974).
- [17] S. Gottesfeld, S. Srinivasan, Optical and electrochemical properties of surface films formed on Pt and Ir in the O_2 evolution region, Extended Abstract, 149th Meeting of the Electrochemical Society, Washington, D.C., May 1976 (BNL 21509).
- [18] G. Bianchi, T. Mussini, Accumulo dell energia elettrica mediante un ciclo di elettrolisi: e ricombinazione in pila a combustibile, Ric. Sci. Rend., 6A, 37 (1964).
- [19] G. Bianchi, The hydrogen-chlorine fuel cell, Premame, 1, 60 (1965).
- [20] G. Bianchi, C. Traini, La pila a combustibile H_2-Cl_2 , Chim. Ind., 46, 363 (1964).
- [21] E. Gileadi, S. Srinivasan, F. J. Salzano, C. Braun, A. Beaufrere, S. Gottesfeld, L. J. Nuttall, A. B. LaConti, An electrochemically regenerative hydrogen-chlorine energy storage system for electric utilities, to be published in the J. of Power Sources (BNL 21820R).
- [22] W. C. Gardiner, Hydrochloric Acid Electrolysis at Wofen (1946).

- [23] F. B. Grosselfinger, New chlorine source: byproduct hydrochloric, Chem. Eng., 71, 1972 (1964)
- [24] P. Gallone, G. Messner, Direct electrolysis of hydrochloric acid, Electrochem. Tech., 3, 321 (1965).
- [25] S. Yoshizawa, F. Hine, Z. Takehara, Y. Kanaya, Studies of hydrogen-chlorine fuel cell. I. Basic studies of the hydrogen-chlorine fuel cell at low temperature, J. Electrochem. Soc., Japan, 30, E10 (1962).

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

AREA 2: HYDROGEN STORAGE SUBSYSTEMS

Scope:

This activity is concerned with the evaluation and testing of various methods of storing hydrogen. The systems portion deals with the preparation of reference designs, with dynamic system modeling, and with correlation of the experimental data in order to develop a reliable design methodology which can be transferred to industry at an early date. The applications portion involves detailed design, construction and testing of metal-hydride test beds for various stationary and land-based vehicle applications. Among the data to be obtained for the design of larger scale equipment by industrial firms are: (a) changes in chemical and physical behavior resulting from long-term cycling; (b) hydriding and dehydriding rates for various types of heat-transfer cells; (c) resistance of container materials to hydrogen embrittlement (or loss of ductility) in a hydride environment; and (d) the behavior of various controls and equipment items in the test system. The service system to be used for testing and evaluating all components of the proposed electric energy storage system is known as the Hydrogen Technology, Advanced-Component Test System (HYTACTS).

2.1 Reference Designs and Process Systems

In conjunction with Burns and Roe, Inc., an architectural engineering firm, a preliminary cost-effective design study [1] was made of the FeTiH_x metal-hydride storage portion of the electrochemical energy storage system for utility load-leveling applications. The results of this study show that for equivalent hydrogen output the vessel cost ranges from about \$7.7/kWh for vessels 1 ft in diameter to \$4.5/kWh when the diameter is 8 ft. By using 3-ft-diameter seamless pipe (largest size available), the longitudinal weld seam can be avoided at a cost penalty somewhat less than the 30% for a welded shell of

this size. Higher costs for the use of the smaller units are mainly due to the greater number of components used in manifolding them.

The following criteria were set up for design of a large metal-hydride storage plant utilizing a hydride of the iron-titanium family:

1. Minimum use of stainless steel or other expensive alloys;
2. minimum number of welds, seals and joints;
3. manufacture to be accomplished by existing fabrication equipment at the rate of 25 storage plants/yr;
4. storage units to be truck- or rail-transportable;
5. storage units to be arranged so as to occupy minimum land area at existing substation sites;
6. minimum capacity to be 90% of plant rating when one storage module is out of service; and
7. number of modules used should be that which minimizes the cost.

The prototype module design resulting from this cooperative study is shown in Figure 2.1. It consists of a conduction-type hydride bed utilizing internal heating/cooling tubes and porous metal tubes (PMT) for distribution and collection of the hydrogen. The module is similar in design to the 10-lb H_2 reservoir previously constructed for testing at Public Service Electric and Gas Company of New Jersey, except that it has a tube sheet.

A preliminary techno-economic study was initiated for the electrochemically regenerative H_2 - Cl_2 system mentioned in Section 1.6. This system is proposed for the load leveling by electric utilities because its efficiency is expected to be more than 50% higher than that of the H_2 - O_2 (air) system previously considered. An additional requirement of this system

is that Cl_2 storage is necessary and, of course, corrosive materials have to be handled. These needs will add to the cost of the system and the safety standards. Because the fuel cell reactants are stored externally, the stored energy is not subject to the limitations imposed by storage batteries. The study is being made in conjunction with industrial firms having experience with electrolyzers and batteries.

The reference design of the $\text{H}_2\text{-Cl}_2$ electric energy storage system assumed for this study consists of the following major components: (1) a solid-polymer-electrolyte (SPE) electrolyzer/fuel-cell stack for high power density and low cost; (2) a hydrogen storage subsystem utilizing a metal hydride of the FeTi family; and (3) a plastic-lined steel tank for storage of the Cl_2 as a liquid in aqueous HCl . A schematic diagram of the proposed system is shown in Figure 2.2. In support of the design and cost study, cell reversibility and optimization are being examined experimentally in conjunction with General Electric Company.

2.2 Hydrogen Technology, Advanced-Component Test System HYTACTS

This system, now being designed, will initially provide the services required for testing the electrochemical and hydrogen storage components of the electric energy storage system. The plan for constructing the HYTACTS is to complete the hydrogen storage section first and to complete the remainder prior to delivery of the electrochemical component by General Electric Company. Subsequently an addition will be made for testing storage components for highway vehicles. The HYTACTS control and process flow diagram for the hydrogen storage section is shown in Figure 2.3.

It was recently demonstrated that the volumetric expansion (10-15%) which occurs during hydriding can cause vessel bulging in a deep bed (see Section 2.5). Two proposed solutions for

this problem will be examined using a 2-ft-diameter test bed designated as the Variable Parameter Test Unit (VPTU). It is a flanged-head vessel capable of testing various internal assemblies and is ~6 ft in length. The first assembly will contain a second set of PMT to be used for periodic loosening of the FeTiH_x bed. Through the use of this technique it is believed that the effect the interparticle friction, which limits expansion to the free surface in deep beds, can be overcome. The plan is to bring the bed to a state of incipient fluidization by a brief flow pulse when hydriding is started; then the volumetric expansion may be accommodated by reduction of the void space and some expansion to the free surface. The second proposed solution consists of supporting the bed on a series of trays of heat-transfer panels using a bed depth which permits expansion to the free surface without bulging of the tray sidewall. In this case, the longitudinal axis of the vessel would be vertical, and although less ground space would be required, a deep pit might be required to maintain a low profile.

It is planned to fabricate the VPTU from a low-carbon steel, which Sandia-Livermore Laboratories has found suitable for hydrogen service at 600 psia, provided that tests in FeTiH_x confirm this result (see Section 2.5 for information on the testing program). The design will be completed in conjunction with an industrial firm having the capability to construct the unit.

2.3 Engineering Test Beds

A 6-in.-diameter test bed, or heat-transfer cell, was constructed and operated in order to obtain data pertinent to the design of a plant-scale energy storage system suitable for load leveling by electric utilities. The storage system utilizes a decomposable metal hydride which absorbs hydrogen, produced electrolytically by off-peak power. Subsequently

the hydrogen is desorbed and flows to a fuel cell where it reacts with the oxygen in air to regenerate power during a period of peak demand. A heat-transfer cell is a basic sub-unit of a hydride reservoir; its behavior is expected to closely approximate that of a large reservoir, a number of which would be required for the energy storage load of an electric utility. A hydride reservoir is a device consisting of a pressure vessel filled with a suitable granular hydride, and provided with a particle barrier, a gas connection and a means of handling the thermal load.

The present reservoir design is based on the concept of canning the hydride in tubes and assembling them in a geometrical array in a water tank, similar to the way in which fuel is arranged in a nuclear reactor. The advantage of having the heat-transport fluid (water external to the cylindrical cell, as opposed to having a water tube on the cell axis, is that the heat-transport fluid is adjacent to the major cross-sectional area of the hydride bed. Thus, if bed activity at the greatest distance from the heat-transport fluid is limited by heat transfer under certain operating conditions, the loss of storage capacity would be considerably less than it would be in the case of a cell having a water tube on its axis. In either case, cooling of the bed is required during hydriding, and heating is required during dehydriding. The water tank for the cell tested was simulated by providing it with a water jacket having a 1/8-in. annulus. The 2.5-ft-long vessel was made from 6-in. pipe and end caps (schedule 10 wall, type 316SS) welded together. An axial porous metal tube, 5/8-in. O.D. with a rating of 0.5 μ M (micron), was used as the particle barrier. The hydride was made from FeTi alloy produced by N.L. Industries (batch NL-2); the 84 lb. of granular alloy (-4, +100 mesh) had a working storage capacity of 1 lb. of H_2 over the composition range $FeTiH_{0.175}$ - $FeTiH_{1.400}$. Internal thermocouples

were used for obtaining axial and radial temperature profiles. A sketch of the cell or test bed is shown in Figure 2.4, and the assembled unit on its test stand is shown between the two panel boards in Figure 2.5. This device was named the ESEERCO Test Bed because the Empire State Electric Energy Research Corporation shared the cost of the program.

In the first series of runs it was determined what length of time various H_2 flow rates could be sustained, for both halves of the hydride-dehydride cycle, under the conditions stated below. The working capacity of a hydride bed is a function of the water temperature used for meeting the thermal load, and the pressure of the external system. During hydriding, cooling water was used at $30^{\circ}C$ ($86^{\circ}F$) and 2 gpm, along with a maximum H_2 charging pressure of 500 psia. High-purity H_2 (99.999%) was used from pressurized gas cylinders. For dehydriding, heating water was used at $50^{\circ}C$ ($122^{\circ}F$) and 2 gpm, and H_2 was released until the bed pressure was close to 16 psia. The time that a given flow rate could be sustained was determined, as was the time needed to transfer 1 lb. of hydrogen, i.e., 5409 liters, for flows of 40, 30, 25, 20, 15, and 10 standard liters per minute (SLPM, at $68^{\circ}F$ and 14.7 psia). Table 2.1 lists these times along with the related pressures, hydrogen flow rates and amount transferred; four of the half cycles were done as two runs. The sustained flow rate data are plotted in Figure 2.6 for the charging part of the cycle, and in Figure 2.7 for the discharging part. The amount of hydrogen transferred during that time is also plotted. These results show that for the water temperatures and terminal pressures used, the ESEERCO Test Bed could sustain a flow close to 9 SLPM for 10 hours over the composition range $FeTiH_{0.175} - FeTiH_{1.400}$. This rate is equivalent to 1.19×10^{-3} lb H_2 /hr-lb FeTi alloy.

Additional details and results for the above runs have been presented in other publications [2,3]. Under these dynamic conditions the amount of hydrogen transferred is about 83% of that estimated from the equilibrium data.

2.4 Metal-Hydride-Material Test Beds

Several 1-in.-diameter test beds were set up to determine the long-term behavior of hydrides of the iron-titanium family during accelerated-cycle tests. The items of interest are any change in hydrogen storage capacity and the increase in pressure drop due to particle attrition. Each test bed was provided with a water jacket for heating and cooling, porous-metal filter discs at each end for particle retention (10- μ M rating), as well as connections for hydrogen transfer and the instrumentation used in controlling and monitoring the process. The hydride was confined to the 12-in. jacketed length of the type 304SS tubing by quartz-wool plugs at each end. Fresh hydrogen having a purity of 99.999% was used for each cycle, and the flow was downward for both parts of the cycle. A typical cycle consisted of hydriding for 30 minutes at $\sim$ 530 psia, with cooling water at 12-15°C (54-59°F), followed by dehydriding for 15 minutes with steam at 110°C (230°F).

Two test beds, A-1-1 and A-1-2, filled with about 350 grams (0.77 lb) of alloy from batch NL-1, were cycled until it was evident that their storage capacity was gradually decreasing. Some in-leakage of air was considered the most likely cause of this deterioration; so bellows-sealed valves were substituted for packed valves, and nearly all of the compression-type fittings were replaced with welded or O-ring joints. Although both sets of equipment were then proven leak-tight using a mass-spectrometer leak detector, there was no recovery of storage capacity. The contents of test bed A-1-1 were sieved after 1439 cycles in order to determine the extent of attrition. The starting material of -10 + 16 mesh size (passed through a 10-mesh/in. sieve and retained on a 16-mesh/in. sieve) had become considerably reduced in size. About 90%

of the hydride suffered a 10-fold reduction in size, and 30% of it passed through a 400-mesh sieve.

Test bed A-1-2 was reactivated after 1661 cycles; and although its capacity was nearly restored, deterioration immediately resumed and operation was stopped after 49 more cycles. In this case the starting material of -80 + 100 mesh size, decreased in size so that after 1710 cycles 59% of the hydride passed through a 400-mesh sieve. Examination of the hydrided material by International Nickel Company, using Auger spectroscopy, showed the presence of a sulfur-containing film which was also found at a much lower level in the FeTi alloy. It had an unexpectedly high sulfur content, 0.048 wt % (average of four analyses), and the hydrided material had 6% more. It seemed unlikely that the hydrogen was contaminated because several batches of cylinders were used. Other alloys have not behaved similarly in the same equipment; consequently it appears that the sulfur in the alloy somehow caused the gradual reduction in storage capacity. The sulfur on the surface was evidently removed during reactivation at 300°C and then built up again. If the 6% increase in sulfur is real, its source is not known.

A modified FeTi alloy, in which some of the Fe is replaced by Mn, was subjected to a cycling test because its properties appear to be more favorable for the electric utility application. It is easily activated, can be charged at a slightly lower hydrogen pressure, and it is expected to have a slightly higher storage capacity. The alloy $\text{TiFe}_{0.7}\text{Mn}_{0.18}$, batch INCO-1 of -16 + 20 mesh size, was used as the starting material in test bed A-3-1. After 102 cycles it was evident from pressure-drop measurements that the attrition was proceeding very rapidly. By then the particle size and pressure-drop data were comparable with that previously obtained for FeTiH_x after 1000 cycles. Further testing was stopped after

207 cycles because the pressure drop had increased to ~ 4 psi/ft. A sieve analysis showed that 95% of the starting material had suffered a 10-fold reduction in size and 66% passed through a 400-mesh sieve. This rapid attrition evidently eases activation because of the increase in surface area upon contact with H_2 . The high pressure drop would probably require a closer spacing of the filter tubes in a full-scale hydride storage unit.

In all of these beds attrition was accelerated due to their depth. The length: diameter ratio for each unit was ~ 12 ; so they can be classed as deep beds. Due to the angular shape of the particles and the expansion which occurs during hydriding, the particles tend to "lock-in" and create shearing forces which cause particles to break up where microcracks exist. In shallow beds there is enough movement to the free surface and attrition is minimal. An important effect of expansion in deep beds is described in the next section.

The same vessel was reused for testing a new FeTi alloy having a lower oxygen content and therefore, presumably, a slower rate of attrition. This alloy, NL-2A, was used in the size range $-10 + 16$ mesh, and the test bed was designated A-1-3. As expected, the alloy was more difficult to activate because of its lower oxygen content. A typical cycle consists of hydriding at 500 psia for 60 minutes using cooling water at $10-15^\circ C$ ($50-59^\circ F$) and then dehydriding to essentially atmospheric pressure for 30 minutes using steam in the jacket at $\sim 118^\circ C$ ($\sim 244^\circ F$). The average change in composition over the cycle is expressed as $\Delta H_x = 1.2$. After 932 cycles the H_2 supply was changed from 1-lb cylinders of 99.999% purity to a supply piped into the building from large cylinders. This 750-lb supply, obtained from Project Mercury as excess material, is of equal or higher purity. Presently the hydride has undergone 3385 cycles with no loss of hydrogen storage capacity.

When the test is concluded after 4000 cycles, or the equivalent of 15 years of operation, the test bed will be examined in detail. Recent pressure-drop measurements have shown a definite leveling off at close to 1 psi/ft, indicating that the rate of particle attrition has also decreased. The results thus far indicate that the hydride will retain its hydrogen storage capacity over a period of years provided high-purity hydrogen is supplied.

2.5 Container Materials Selection

Although types 304 and 316 stainless steel have performed satisfactorily as container materials for the FeTi family of hydrides, they are too costly to use for large vessels. A search for economical materials is underway in cooperation with Sandia Laboratories (SL). Screening tests performed there in 600-psi hydrogen identified several candidate materials for further testing in an FeTiH_x environment. An agreement was made that BNL would build the equipment and expose the specimens supplied by SL, and that the specimens would be examined at SL after an exposure to hydride-dehydride cycling for about six months. The effect of hydrogen embrittlement or loss of ductility will be evaluated by stressing each specimen to failure and measuring the percent reduction in area. The amount of decrease in the value for a smooth bar specimen is a measure of its hydrogen sensitivity.

The materials recommended by SL were: carbon steels A516 grade 70 and A106B, low-alloy steel 2 1/4 Cr-1/2 Mo, aluminum alloy 6061 T6 and stainless steel type 304; the latter two were included for reference. Provision was made for loading 80 specimens in the hydride bed by stacking them in eight cylindrical cages made of wire. This test bed was designated the Container Materials Test Bed (CMTB); it was fabricated from 6-in. pipe and two end caps welded together and is about 30 in. long. The materials were supplied in the form of 80

self-loaded tensile specimens at two stress levels. Some of the specimens were plain and other contained welds, notches and a Sn-Pb solder coating for reducing hydrogen diffusion. The test matrix is given in Table 2.2.

There was a delay in exposing the specimens to FeTiH_x ; so they were blanketed with argon after being loaded in the vessel. The main reason for the delay was due to addition of an expansion test made during activation of the FeTi alloy (batch INCO-3 produced by International Nickel Company). For this test a vessel of similar design was used, and the alloy was poured into the vertically mounted bed to a depth of 22 9/16 in. (3.5 diameters); no attempt was made to loosen the bed and thereby minimize the effect of volumetric expansion upon hydriding. Previously test beds had been activated with the axis of the test bed horizontal and with occasional oscillation to keep the bed loose. Not unexpectedly, expansion occurred in all three dimensions, the support plate was dished downward about 0.25 in.; the surface elevation increased about 1.5 in.; and the average increase in diameter at the plane of maximum bulging was 0.080 in., as determined by measurement of the change in circumference. Subsequently measurement of the 6-in.-diameter ESFERCO Test Bed, which had been activated horizontally and then carefully positioned vertically, showed that it had bulged only 0.0064 in. after a total of 30 hydride-dehydride cycles. Thus it appears that initial loose packing only reduces the rate of bulging, and some means is required to accommodate the volumetric expansion which is close to 15%.

Following this test, the Activation Vessel (AV) was coupled to the CMTB and the hydrided material was physically transferred by inverting the AV. The vessels were disconnected after valving off the CMTB and preparations were made for starting the exposure to hydride-dehydride cycling.

2.6 Pressure Drop in Packed Beds

The extensive attrition which decomposable metal hydrides suffer upon long-term hydride-dehydride cycling causes a large increase in pressure drop, thereby controlling the design of the filter system in the bed. Granular FeTiH_x particles a few millimeters in size are gradually reduced to a powder so that by the end of 4000 cycles the average particle size is estimated to be only 10 μM (microns). This decrepitation is due to embrittlement of the hydrided material and the effect of volumetric expansion, especially in deep beds--those several column diameters deep. The particles are angular in shape and tend to interlock; thus there is a limited amount of expansion to the free surface. In rubbing against each other the particles fracture where microfissures have developed and the local stresses are sufficiently high. Thus, the pressure drop for hydrogen flow can increase from a few inches of water head to the psi range upon extended cycling in deep beds. In order to avoid excessive pressure drop in the bed, it is necessary to provide a geometrical array of porous metal tubes (PMT) and to specify their number, porosity and diameter.

A simple apparatus was set up for measuring the pressure drop of hydrogen flowing through beds of known particle size and void fraction. Glass graduated tubes (200 and 250 ml) were used as containers in order to facilitate observation of the bed height. Each tube was provided with a coarse filter frit, for support of the bed, and gas inlet and outlet connections. Various packing densities were attained through the use of a "Tap-Pak Volumeter" (TPV), a device which provides a series of axial taps to the base of the container. This device has a platform to which the base of the container is clamped; and its counter can be set to provide a fixed number of taps (up to 99,999) at the rate of 2.5/sec. The pressure

drop range was limited by the mercury manometer height and the strength of the glass containers (about 2 atm.). Hydrogen flow was controlled by a micrometer needle valve, was measured by a thermal mass flowmeter, and was downward in order to avoid loosening the bed at high flow rates. Pressure-drop measurements were generally made over the flow range 0.448 to 21.9 SCFM/ft² with various batches of bed material ranging in size from 5 to 45 μ M. Dehydrided FeTiH_x or FeTi alloy was used, with one exception. Fine SiC powder was substituted in order to have enough material close to an average particle size of 5 μ M. This material has the same general particle shape and surface character as FeTi.

For a given material, the experiments were made in order of increasing bed density, and air was thoroughly flushed from the system prior to taking data. When the maximum pressure drop was reached for each bed density, the void fraction was further reduced by operating the TPV until the desired value was obtained, and another set of data were taken. The experimental and calculated values for the differential pressure--flow rate relationship are shown in Figure 2.8 for two void fractions, 0.550 and 0.582. Other investigators have found that this relationship is linear for laminar flow conditions and particles somewhat larger than 45 μ M, [4,5,6]. The equation selected for calculation of the pressure drop was one used for flow through a porous metal wall because it provided the closest agreement with the experimental results [7]. For the range of test conditions used, the agreement was within 6%. In rearranged form the equation which relates the various particle, fluid and container parameters is:

$$P_u = \frac{\left[\frac{\alpha t \mu \rho_s RT Q}{30} + P_d^2 \right]^{0.5}}{t} - 14.7 \quad (1)$$

where

$$\alpha = \left[\frac{(1-\epsilon)^{0.7}}{\epsilon^3 K D_p \phi_s} \right]^2$$

The above relationship for α , the viscous resistance coefficient, was derived empirically, whereas it was previously obtained experimentally. In the original equation, the term containing β , the inertial resistance coefficient, was so small that it was neglected.

- P_u = Upstream pressure, psi/in.
- P_d = Downstream pressure, psi
- Q = Fluid flow-rate, SCFM/in.²
- R = Gas constant, 2.4654×10^4 ft-lb/SLUG-°F
- t = Bed height, in.
- T = Temperature, °R
- μ = Fluid viscosity, SLUGS/in.-sec.
- ρ_s = Fluid density at STP, SLUGS/ft³
- α = Viscous resistance coefficient, in.⁻²
- D_p = Average particle diameter, microns
- K = Empirically derived constant, 6.94×10^{-6}
- ϵ = Void fraction, dimensionless
- ϕ = Particle shape factor, dimensionless

A computer program was used for calculation of differential pressure vs. particle diameter at four flow rates for a fixed void fraction (0.57) and bed height (5.58 in.). As shown in Figure 2.9, the differential pressure increases rapidly for particle sizes smaller than about 20 μ M. Thus for a flow of 2.49 SCFM/ft² and the average particle diameter at 4000 cycles, the differential would be slightly more than 2 psi/in. of bed for material having a void fraction of 0.57. Additional details and all of the experimental data are given in Reference [8].

Subsequently, the above equation was used for specifying the arrangement of PMT in the 2-ft-diameter FeTiH_x reservoir to be tested in the Hydrogen Technology Advanced Component Test System (HYTACTS). For hydrogen flow rates of 1.36 SCFM/ft and 2.72 SCFM/ft², which are for 10- and 5-hour operating periods, the PMT details specified were: 6 PMT uniformly spaced at a radius of 8.5 in., plus 1 PMT on the vessel axis; 5/8-in. O.D.; and 0.5 μM porosity rating. The calculated pressure drops in the bed, for the 10- and 5-hour operating periods, were 7.3 and 11.9 psi; and the pressure drops through the PMT walls for the same periods were 0.23 and 0.44 psi. All of the pressure drops are independent of the vessel length because the hydrogen flow is normal to the PMT and vessel axis.

Table 2.1

Summary of ESEERCO Test Bed Data for Sustained-Flow-Rate Runs^a

ESEERCO	Constant Flow Rate Period					Variable Flow Rate Period				Totals	
Run No.	P ₁ PSIA	Rate SLPM	Time Min	Wt Lb	P ₂ PSIA	Time Min	Wt Lb	P ₃ PSIA	Rate SLPM	Wt Lb	Time Min
E03C1	71.7	40	72	0.532	496	179	0.375	501	3.83	0.907	251
E03C2	266	20	15	0.0565	493	69	0.0355	499	1.41	0.092	84
E03D1	499	40	79	0.579	26.4	169	0.454	16.2	6.60	1.033	248
E03D2	55.4	10	11	0.0200	20.9	2	0.0037	18.2	8.85	0.0237	13
E04C1	39.7	30	115	0.648	492	169	0.331	498	4.13	0.979	284
E04D1	492	30	115	0.635	28.8	133	0.332	16.9	6.80	0.968	248
E04D2	51.5	10	12	0.0214	18.4	2	0.0031	17.1	6.88	0.0246	14
E05C1	37.3	25	162	0.751	494	153	0.250	500	3.87	1.001	315
E05D1	504	25	154	0.712	26.1	117	0.258	16.7	6.33	0.970	271
E05D2	57.6	5	33	0.0309	18.3	0	0	--	--	0.0309	33
E06C1	28.5	20	224	0.832	498	116	0.168	501	3.81	1.000	340
E06D1	503	20	214	0.796	23.1	127	0.204	16.0	4.13	1.000	341
E07C1	32.0	15	324	0.903	499	84	0.097	500	3.49	1.000	408
E07D1	511	15	315	0.878	20.3	87	0.122	15.8	3.72	1.000	402
E08C1	30.2	10	519	0.967	498	36	0.033	498	3.61	1.000	555
E08D1	502	10	510	0.951	18.0	55	0.049	15.6	2.73	1.000	565

^a For batch NL-2 of FeTi alloy. H₂O conditions: 2 GPM, 30°C (86°F) for charging, 50°C (122°F) for discharging. In the Run No. C = Charging and D = Discharging.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

Figure 2.1 Burns and Roe prototype module design.

Figure 2.2 H_2 - Cl_2 Electrochemical Energy Storage Power Plant Schematic.

Figure 2.3 HYTACTS Flow Diagram for the Hydrogen Storage Section.

Figure 2.4 Sketch of ESEERCO Test Bed.

Figure 2.5 View of ESEERCO Test Bed operating area.

Figure 2.6 ESEERCO Test Bed performance during hydriding.

Figure 2.7 ESEERCO Test Bed performance during dehydriding.

Figure 2.8 Pressure drop vs. hydrogen flow rate through a fixed bed.

Figure 2.9 Pressure drop vs. particle size for hydrogen flow through a fixed bed.

Area 2: Hydrogen Storage Subsystems

References

- [1] Conceptual Design Study of a Metal Hydride Storage Power Plant, report prepared for Brookhaven National Laboratory by Burns and Roe, Inc., Hempstead, New York, February 1976.
- [2] G. Strickland, J. Milau, Wen-Shi Yu, The behavior of iron titanium hydride test beds: long term effects, heat transfer and modeling, Proceedings of the First World Hydrogen Energy Conference, Miami Beach, Florida, March 1-3, 1976. (BNL 20876)
- [3] G. Strickland and Wen-Shi Yu, Some Rate and Modeling Studies on the Use of Iron-Titanium Hydride as an Energy Storage Medium for Electric Utility Companies, February 1977. Formal Report. (BNL 50667)
- [4] Abraham Lapin, Pressure drop for gases flowing across packed beds, Chem. Eng. Prog., 58, July 1962, 47-52..
- [5] Max Leva, Pressure drop through packed tubes, part 1, Chem. Eng. Prog. Trans., 43, October 1947, 549-54.
- [6] M. Leva and Milton Grummer, Pressure drop through packed tubes, part 2, Chem. Eng. Prog. Trans., 43, November 1947, 633-38.
- [7] Mott Metallurgical Corp., Farmington, Connecticut, Catalog 1000, p. 6.
- [8] M. J. Rosso, G. Strickland, J. Milau, Pressure Drop--Flow Correlations for Fixed Beds of Small, Irregularly-Shaped Particles, November 1976. (BNL 50589)

AREA 3: HYDRIDE MATERIALS DEVELOPMENT

Scope:

Establish a set of chemical and physical specifications for iron-titanium and substituted iron-titanium alloys. These specifications are to include such information as partial pressure of hydrogen, particle attrition due to hydriding-dehydriding, flow and pressure-drop characteristics, sensitivity to impurities, and other properties relevant to use in hydrogen storage systems.

When preliminary specifications are available, begin to identify and develop the capabilities of a manufacturer to supply the quantities required for the engineering test facilities.

3.1 Pressure-Composition Relationships

In order to more satisfactorily match the operating parameters of the H_2 - O_2 energy storage system, a series of experiments was carried out with manganese-containing ferrotitanium alloys of the type $TiFe_yMn_x$. In general, hydrides of these alloys are more stable (thermodynamically) than those without Mn. Of this class of Mn substituted alloys, $TiFe_{0.7}Mn_{0.2}$ was chosen as the most promising candidate to replace FeTi in the reference design hydrogen reservoir on the basis of the pressure-temperature-composition (P-C-T) data for the hydride. The plots are shown in Figures 3.1 and 3.2 for this material; those for other hydrides studied are shown in Appendix A as Figures 3A1 through A9. A substantially higher attrition rate was measured for $TiFe_{0.7}Mn_{0.2}H_x$ than for Mn-free hydride. This behavior was attributed to the presence of secondary phases precipitated by the Mn. It was found that a composition corresponding to $TiFe_{.76}Mn_{.14}$ resulted in a single-phase alloy which can be expected to be more resistant to attrition, and thus be more attractive for practical purposes. Accordingly, a series of experiments was carried out close to this composition, and

desorption isotherms were measured for the ternary system $\text{TiFe}_{0.762}\text{Mn}_{0.136}\text{-H}$ at 30, 40, 50, 100 and 120°C and for the $\text{TiFe}_{0.762}\text{Mn}_{0.138}\text{-H}$ system between 30-50°C. The results of these measurements are shown in Figures 3.3 and 3.4. Sorption isotherms were also obtained for these alloys at 40°C. The sorption and desorption isotherms of these two systems at 40°C are plotted in Figures 3.5 and 3.6, and illustrate the hysteresis at this temperature. A desorption isotherm at 40°C, shown in Figure 3.7, was also measured for the substituted ferro-titanium alloy of composition $\text{TiFe}_{0.79}\text{Mn}_{0.15}$ produced by the International Nickel Corporation (INCO-2). Examination of the P-C-T relationships of these Mn-containing materials revealed that a slight variation in the composition, around the single-phase region, can cause a considerable change in the P-C-T characteristic. This point is illustrated in Figure 3.8 which also shows the desorption isotherm for pure FeTi.

Isotherms were also obtained on a few other miscellaneous alloys. These were: (1) high-purity, arc-melted FeTi (referred to as NL-2), (2) FeTi (obtained from Daimler-Benz Corp.), (3) Mischmetal de-oxidized FeTi (INCO-3), and (4) $\text{TiFe}_{0.76}\text{Mn}_{0.143}$. Sorption P-C-T data was measured for FeTi (NL-2) at 30 and 50°C, whereas desorption isotherms were obtained at 40°C for the Daimler-Benz material and at 100 and 120°C for $\text{TiFe}_{0.76}\text{Mn}_{0.143}$. The INCO-3 sample was run as a desorption isotherm at 40°C and is shown in Figure 3.9.

Recently, work was initiated on synthesizing several less stable Mn-substituted TiFe-H systems for use as hydrogen storage media in conjunction with an HCl electrolysis cell. Because the current design specifications for this HCl unit call for available waste heat at approximately 85°C, a less stable alloy-H system is necessary. The first candidate tested was $\text{TiFe}_{0.9}\text{Mn}_{0.15}$, which forms a slightly more stable hydride. Experiments were

initiated on determining the minimum initial activation temperature necessary for ternary substituted FeTi alloys containing Mn. As shown in Table 3.1, these alloys can be activated at room temperature or slightly above, whereas FeTi requires heating to 300°C. A slight variation around the single-phase composition, as indicated by the INCO-1 sample and the $\text{TiFe}_{0.7}\text{Mn}_{0.2}$ material, can also lead to significant effects on the ease of activation.

3.2 High-Cycle Testing

The materials development program is not only concerned with P-C-T relationships, but also with certain other system properties which are very important with respect to the performance of a practical hydrogen storage reservoir. These are:

- (1) The physical attrition of the alloys as a function of the number of hydriding-dehydriding cycles;
- (2) the activity of the alloy toward hydrogen as a function of the number of such cycles; and
- (3) the poisoning effect of impurities such as O_2 , N_2 , CO , etc., in the hydrogen gas.

In order to investigate these variables a laboratory high-cycle test apparatus was built.

Several alloy samples were subjected to high-cycle testing in a closed loop: high-purity FeTi (NL-2) and three Mn-containing ferrotitanium alloys. Pertinent data concerning these experiments are given in Table 3.2 and Table 3.3. It was evident from these tests that there is no inherent deterioration of alloy activity toward hydrogen as a function of the number of hydriding-dehydriding cycles, provided pure hydrogen (99.999%) is used. In this connection, several quantitative experiments were carried out investigating the poisoning effect of oxygen in the hydrogen gas phase. The results of these experiments are graphically illustrated in Figures 3.11 through 3.14. The results can be summarized by noting that FeTi is very sensitive to the presence

of oxygen; as little as 10 ppm O_2 in hydrogen will have a measurable and negative effect on the reaction kinetics. However, it was possible in all cases to restore the alloy to its original state by subjecting it to the usual activation procedure.

With respect to the rate of physical attrition (Table 3.3) the highest rate occurred in the first few cycles after which it slowed considerably. It was also apparent that pure FeTi is much more resistant to physical attrition than any of the ternary manganese alloys. In this connection, it should be noted that the FeTi sample was removed after 19,568 cycles. Qualitative examination indicated that while a substantial decrease in particle size occurred, it was not of a magnitude which would constitute a serious engineering problem. This sample is now undergoing extensive physical and chemical characterization.

3.3 International Nickel Corp. Subcontract, "The Interrelations Among Composition, Microstructure and Hydriding Behavior for Alloys Based on the Inter-metallic Compound FeTi"

The first year of this subcontract ended and an annual report was received. The report summarizes work performed from the start of the contract (April 14, 1975) to mid-April 1976. The more important conclusions resulting from this work are listed below:

1. The hydriding properties of FeTi, and related alloys are intimately related to composition and microstructure.
2. Oxygen contamination of FeTi leads to the formation of an O-rich phase of the approximate stoichiometry $Fe_7Ti_{10}O_3$. Because this phase does not hydride, its presence drastically reduces the hydrogen storage capacity of FeTi. The presence of large amounts of $Fe_7Ti_{10}O_3$ increases the second stage activation rate by lowering the fracture toughness of the FeTi matrix.

and providing preferred paths for hydride penetration. In a similar manner, $\text{Fe}_7\text{Ti}_{10}\text{O}_3$ tends to promote decrepitation (particle size breakdown) during cycling. In general, melting procedures should aim at minimizing the final O-content of the alloy (<1000 ppm).

3. Mn and Cr substitute at least partially for Fe in FeTi. However, direct atom-for-atom substitution of Mn or Cr for Fe in FeTi promotes the formation of some Fe_2Ti . To minimize this effect and maximize storage capacity, Mn- or Cr-containing storage alloys should be slightly Ti-rich.
4. Ni substitutes directly for Fe on a one-to-one atom basis without changing the microstructure of FeTi.
5. V probably substitutes for Ti in the FeTi structure.
6. Increasing the Ti content, or partial substitution of Mn, Cr, V and Ni, lowers the dissociation pressure of FeTi hydride. This behavior can be correlated with the lattice parameter of the cubic FeTi crystal structure, and can be qualitatively interpreted in terms of bonding changes in the inter-metallic compound and the "Rule of Reversed Stability."
7. Slightly Ti-rich Ti-Fe-Mn alloys represent a promising extension of the FeTi alloy for hydrogen storage applications. The alloys are metallurgically more complex than FeTi and need optimization. Various preliminary correlations among composition, microstructure, and hydriding behavior have been developed for the slightly Ti-rich Ti-Fe-Mn system.
8. Examination of a 1-kg FeTi sample hydrogen cycled 1500 times in an engineering test bed at BNL indicated that the reason for slow deactivation

was surface poisoning from sulfur, probably a trace impurity in the H_2 used or an S-containing compound in the experimental system. The general area of surface poisoning is a critical one and deserves further study.

9. Examination of a $TiFe_{0.80}Mn_{0.18}$ sample cycled 1100 times suggests metallurgical phase instabilities are occurring in this alloy with cycling.
10. FeTi cannot be vacuum induction melted in MgO , Al_2O_3 , or ZrO_2 crucibles without significant crucible attack and resultant melt contamination.
11. FeTi, and related alloys, can be vacuum induction melted in high-purity graphite crucibles without significant contamination. The hydriding properties of alloys so melted seem to be fully equal to alloys commercially melted by the cold-crucible, consumable-arc process.
12. High quality FeTi, and related alloys, can be prepared by air melting in clay-graphite crucibles and deoxidizing with rare-earth elements. Mischmetal is the most effective (and lowest cost) rare-earth deoxidant for this purpose. Alloys so produced by this relatively low-cost method seem to have hydriding properties fully equivalent to commercial arc-melted material. The presence of a rare-earth-rich phase in the microstructure promotes activation.
13. The interrelations between metallurgy and hydriding behavior examined for FeTi probably have a general application to other rechargeable hydride systems.

Table 3.1

Minimum-Temperature Activation Experiments

<u>Sample</u>	<u>Maximum Temperature (°C)</u>	<u>Room-Temperature Time at 500 psi (hr)</u>	<u>Final H/M</u>
TiFe _{0.7} Mn _{0.2}	50	3.5	0.94
TiFe _{0.77} Mn _{0.09}	25	27.5	0.98
TiFe _{0.73} Mn _{0.13}	25	19.0	0.98
TiFe _{.70} Mn _{.18} (INCO-1)	25	25	0.91

Table 3.2

High-Cycle Test of Three Hydrides

<u>Material</u>	<u>Complete Cycles</u>	<u>Temperature Change/Cycle °C, Avg.</u>	<u>Pressure Change/Cycle psia, Avg.</u>	<u>Composition Change/Cycle $\Delta H/Ti$, Avg.</u>
FeTi	19568	-1 to +100	428-459	1.11
TiFe _{.79} Mn _{.15} (INCO-2)	28411	-1 to +100	179-211	1.08
TiFe _{.76} Mn _{.14}	26319	-1 to +100	87-114	0.96

Table 3.3

Particle Size Distribution for
 $\text{TiFe}_{0.7}\text{Mn}_{0.18}$ (INCO-1) and FeTi (NL-2)
 As a Function of Hydriding-Dehydriding Cycles

Screen Classification, Mesh	Weight Percent		
	$\text{TiFe}_{0.7}\text{Mn}_{0.18}^*$		FeTi*
	5 Cycles	1115 Cycles	5478 Cycles
+ 16			11.4
+ 20			2.9
+ 30			2.1
+ 40			4.3
+ 60	5.3	6.4	14.7
+ 80	2.0	0.6	16.4
+100	1.5	2.1	11.0
+140	10.1	12.4	-
+200	32.2	25.5	23.0
+275	19.3	21.5	4.2
+325	17.1	11.8	2.3
-325	14.1	19.7	7.7

*Initial particle size range -10 +16 (U.S. Standard Sieve).

Figure 3.1 Pressure-composition desorption isotherms for the TiFe_{0.7}Mn_{0.2}-H system at several temperatures.

Figure 3.2 Hysteresis in the $\text{TiFe}_{0.7}\text{Mn}_{0.2}\text{-H}$ system at 30°C .

Figure 3.3 Pressure-composition desorption isotherms for the $\text{TiFe}_{0.762}\text{Mn}_{0.136}$ -H system at several temperatures.

Figure 3.4 Pressure-composition desorption isotherms for the $TiFe_{0.762}Mn_{0.138}$ -H system at several temperatures.

Figure 3.5 Hysteresis in the $\text{TiFe}_{0.762}\text{Mn}_{0.136}\text{-H}$ system at 40°C .

Figure 3.6 Hysteresis in the $TiFe_{0.762}Mn_{0.138}-H$ system at $40^\circ C$.

Figure 3.7 Pressure-composition desorption isotherms for the $TiFe_{0.79}Mn_{0.15}-H$ system (INCO-2) at 40°C.

Figure 3.8 A comparison of pressure-composition desorption isotherms for alloys of similar composition at 40°C.

Figure 3.9 Pressure-composition desorption isotherms for the FeTi-H system (INCO-3) at 40°C.

Figure 3.10 Pressure-composition desorption isotherms for the $TiFe_{0.9}Mn_{0.1}$ -H system at 85°C.

Temp.

Pressure

Figure 3.11 High-cycle test showing effect of 1.1 mol % O_2 in hydrogen. The amplitude of the right-hand trace is proportional to the activity of FeTi to hydrogen.

Figure 3.12 High-cycle test showing effect of 0.10 mol % O_2 in hydrogen. The amplitude of the right-hand trace is proportional to the activity of FeTi to hydrogen.

Temp.

Pressure

Figure 3.13 High-cycle test showing effect of 0.011 mol % O_2 in hydrogen. The amplitude of the right-hand trace is proportional to the activity of FeTi to hydrogen.

Temp.

Pressure

Figure 3.14 High-cycle test showing effect of 0.001 mol % O_2 in hydrogen. The amplitude of the right-hand trace is proportional to the activity of FeTi to hydrogen.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

AREA 4: NATURAL GAS SUPPLEMENTATION

The work of the Ad Hoc Committee studying "Hydrogen as a Natural Gas Supplement" was completed. This committee was established to study the possibility that hydrogen produced from existing electric generating equipment could be used to supplement the supply of natural gas. Participation in the study group was solicited from a broad base of electric, electric and gas, and gas-transmission distribution utilities, related trade associations, government agencies and the national laboratories in order to attain a balance of views and diverse perspectives on the value of the proposed project. This activity formally began at an organizational meeting held at ERDA Headquarters on April 21, 1976.

In essence, the committee was to decide if hydrogen produced by electric utilities could be used as a source of energy to supplement existing natural gas supplies in the mid-term time frame from the year 1985 to 2000. By June 3, 1976, the committee had defined its charge and was organized into five task groups, each representing the key questions to be addressed by the study. The key question was whether it is appropriate to recommend government support for such a demonstration. This demonstration project was envisioned as a joint government-utility-industry venture.

The following task groups were involved in the study:

- . Motivation
- . Supply
- . Interface
- . Transmission and Distribution
- . Utilization

A supporting group on economic evaluation was formed halfway through the study.

A brief summary of the essential conclusions and recommendations of the Ad Hoc Committee is given below.

Synthetic natural gas derived from coal is presently estimated to be a less expensive supplement to natural gas than electrolytic hydrogen. In addition to being more expensive than synthetic natural gas, the total quantity of electrolytic hydrogen which can be produced from available electric sources is limited to a small fraction of the gas supply, i.e., less than 3% by energy content.

Due to the limited market penetration potential identified by the Ad Hoc Committee, and the uncertain economics relative to SNG, no specific demonstration of this concept is recommended by the committee at this time.

Except for production technology, there are no major technical or safety issues to be resolved in implementing this concept. Gas blends of up to 10 volume % of hydrogen can be accommodated in existing systems. Some regulatory and pricing problems may have to be resolved before implementation. Hydrogen may have more value as a chemical commodity than as a supplement to natural gas; and the concept of direct utilization in the chemical process industry should be further evaluated. Hydrogen is recognized to have a prospective longer-range role in the U.S. energy system as a secondary energy carrier.

Present R&D programs relevant to the near and long-term role of hydrogen are preparing the technology base for utilization of hydrogen; however, these efforts should be focused more on prospective applications. Work on hydrogen production should consider the availability of renewable energy resources and low-cost, base-load electricity.

AREA 5: HYDROGEN STORAGE SYSTEMS ANALYSIS

Scope:

Investigate the expected benefits to the national energy system due to the commercialization of various energy storage technologies in general, and hydrogen systems in particular. Study energy storage options as functions of fossil fuel prices and availability, device cost and availability, and off-peak power supply and cost. Analyze the national impacts of storage technologies commercialization, in terms of total cost, electric and non-electric fuel supply mix, electric load factors and environmental emissions. The results are to be suitable for guiding ERDA RD&D programs and for assisting in energy policy formulation in relation to hydrogen and other storage technologies.

5.1 Studies and Assessments

The systems analysis activities in the area of electric energy storage and hydrogen energy systems included the following studies and assessments.

- A. A general study of the break-even capital costs for electric storage devices was completed [1]. This study did not focus on any one technology, but looked at storage devices as "black-boxes" having variable efficiency and cost. The maximum allowed capital costs for these black-box storage devices are calculated as functions of the following variables:

1. The price of oil
2. The amount of nuclear capacity and the cost
3. The cost and efficiency of alternative peak generation devices, e.g., gas turbine
4. The cost of off-peak electricity
5. Alternative markets for off-peak power

6. The life and efficiency of the storage device
 7. Considering only the electric utility sector of the national energy system.
- B. A study of the economics of introducing fuel cells burning different fuels into the electric sector of the national energy system was completed [2,3]. Four types of fuel cell fuels were considered: distillate oil, natural gas, electrolytic hydrogen, and coal-derived hydrogen. In the case of electrolytic hydrogen, the entire electric energy storage system was considered.
- C. Detailed break-even analysis of dual-mode devices was performed as a function of the electrolytic-hydrogen distribution between the electric and gas sectors, and the ratio of fossil fuels to hydrogen burned by the dual-input fuel cell [4]. The impacts of varying the price of distillate oil and natural gas on the economics of various combinations of dual-mode devices were also considered in that study.
- D. An additional study related to the economic incentive for energy management in buildings was completed [5]. Four basic technologies were considered: improving the overall efficiency of oil-fueled space heating devices, insulation of existing and new masonry structures, dynamic operation strategy for insulated buildings, and utilization of off-peak electric power in conjunction with thermal storage devices for space heating. As an additional part of this work, the availability of off-peak power in the future was estimated, based on the ERDA-48 energy scenarios [6].

- E. A report comparing the economics of hydrogen production by water electrolysis and by thermochemical water splitting was prepared [7]. The report contains parametric comparisons of hydrogen production costs using these two technologies and indicates the range of parameters where similar hydrogen manufacturing prices are projected.
- F. A study of a hydrogen-chlorine electric energy storage system was conducted [8]. The proposed electrochemically-regenerative, closed-cycle system involves: (1) using off-peak power to electrolyze hydrochloric acid; (2) metal hydride storage for hydrogen, and storage of chlorine as a liquid or as the hydrate; and (3) combining the hydrogen and chlorine in a fuel cell for peaking operations and storing the hydrochloric acid for reuse. The main advantages of such a system are: (1) the electrode reactions of hydrogen and chlorine are quite reversible; thus, the overall efficiency (electric-to-electric) can be higher than 70%; (2) the same electrodes can be used as electrocatalysts in both modes (chemical and electricity generation); therefore, the same electrochemical cell can be used for both functions, thereby reducing the capital costs; and (3) it should be possible to use the same cell for electrolysis of water to produce hydrogen and oxygen, at a high efficiency using off-peak power. The expected investment costs of the hydrogen-chlorine energy storage plants were compared with the allowed costs of the generalized "black-box" storage devices which were computed in earlier studies. It was found that for electric-to-electric conversion efficiencies of 0.70 to 0.80, the break-even costs

were \$700/kW(e) to \$750/kW(e), respectively. The fact that the allowed costs of the hydrogen-chlorine plant are higher than the expected investment costs indicates that it should be economical to bring these storage plants into the future (year 1985) electric-generating mix of the United States. These electric storage plants will be introduced so as to displace the less economical peaking-power plants as fuel costs increase.

The annual and unit operating costs of hydrogen-air and hydrogen-chlorine energy storage plants were computed and compared. It was found that the hydrogen-chlorine plant production costs are 40-45% lower than those for the hydrogen-air plant. Both energy storage plants were found to supply more expensive electricity than gas turbines, when operated as peaking devices only, due to the relatively large capital-cost projections and low plant utilization. Reduction in capital costs of the storage device, credit from the hydrogen production for industrial purposes and the expected improvements in the conversion efficiency of the hydrogen-chlorine system (above 70%), will make it an economical and a likely candidate for electric utility peak- and intermediate-load applications, compared with gas turbines burning expensive distillate oil.

- G. A study on the economic and systems incentives for hydrogen injection into the natural gas pipelines was conducted [9]. Initial estimates of expected natural gas shortfall, specifically in the Northeastern United States, and the availability of relatively inexpensive off-peak nuclear power in this region, were made.

The study on the use of hydrogen as a natural gas supplement dealt mostly with the economics of hydrogen production for industrial applications. Two basic technologies were compared: water electrolysis and coal gasification. Meaningful comparison requires a common costing methodology and common basic data. A hydrogen costing methodology that considers first-year costs, and lifetime-averaged costs under inflationary conditions, was developed and utilized. Assuming commercialization of advanced gasification and electrolysis technologies by 1985, the availability of cheap coal for gasification and nuclear off-peak power for electrolysis, it was found that coal-derived hydrogen will cost $\$4.5/10^6$ Btu, whereas electrolytic off-peak hydrogen will cost $\$5.5/10^6$ Btu. Electrolytic hydrogen produced with spinning-reserve power, which is of very limited supply, was projected to be more economic, when obtainable, and to cost about $\$4.0/10^6$ Btu. The relative merits, from a national fuels point of view, of using hydrogen to supplement natural gas supplies, or of using hydrogen as a direct industrial feedstock substituting for natural gas, which is released for other uses, were discussed.

- H. A final draft report of the national hydrogen energy assessment was prepared [10]. This report deals with the expected role of hydrogen within the national energy system, until the year 2000. Recommendations for ERDA RD&D programs in the area of hydrogen energy systems were included. It was recognized in the report that hydrogen is an important industrial chemical feedstock in the petroleum, ammonia, methanol,

and other industries. National fuel policy considerations may require the substitution of current manufacturing technologies, based on natural-gas reforming and residual-oil partial oxidation, by new processes based on coal gasification and water electrolysis. Currently, there is a limited demand for electrolytic hydrogen in the manufacturing industries; but demand will increase if hydrogen is utilized as a natural gas supplement and as a medium for electric energy storage.

The demand for coal-derived hydrogen is expected to increase in the future if a synthetic coal-derived gaseous and liquid fuels industry is established, because hydrogen is an essential captive intermediate in these manufacturing processes. Coal-derived hydrogen has been shown, in a study conducted by Exxon Research and Engineering Company [11], to be more economic by 1980 and thereafter, in comparison with natural-gas reforming and resid partial oxidation, for the production of ammonia and methanol. A summary of the BNL analysis of hydrogen production costs is given in Table 5.1. Based on this information, a cost benefit computation indicated the allowed ERDA RD&D funding levels for the gasification and electrolysis technologies. Other production processes based on thermochemical cycles or solar conversion are not expected to be commercially available before the end of this century and should continue to be funded at relatively lower levels.

Table 5.1

COMPUTATION OF HYDROGEN PRODUCTION COSTS BY VARIOUS TECHNOLOGIES IN THE YEARS 1985 AND 2000
1975 Dollars

Performance and Cost Items	Methane Steam Reforming (1) (5)	Resid Partial Oxidation (1) (5)	Coal Gasification		Lurgi Water Electrolyzer Using Off-Peak Power (2) (4)	SPE New Water Electrolysis		
			Koppers Totzek (1) (5)	Improved K-T (1) (5)		Off-Peak Power (3) (4)	Spinning Reserve (3) (4)	Dedicated Plant (3) (4)
Plant Cost (10^6 \$)	40.7	103.5	160.1	130.0	17.1	0.75	0.75	0.75
Plant Production	100 $\frac{\text{MSCF}}{\text{Day}}$	100 $\frac{\text{MSCF}}{\text{Day}}$	100 $\frac{\text{MSCF}}{\text{Day}}$	100 $\frac{\text{MSCF}}{\text{Day}}$	53.3 MWth	5 MWth	5 MWth	5 MWth
Annual Operation	330 $\frac{\text{Days}}{\text{Yr}}$	330 $\frac{\text{Days}}{\text{Yr}}$	330 $\frac{\text{Days}}{\text{Yr}}$	330 $\frac{\text{Days}}{\text{Yr}}$	55 $\frac{\text{Hours}}{\text{Week}}$	55 $\frac{\text{Hours}}{\text{Week}}$	7920 $\frac{\text{Hours}}{\text{Year}}$	109 $\frac{\text{Hours}}{\text{Week}}$
Annual Average Load Factor	0.904	0.904	0.904	0.904	0.33	0.33	0.904	0.65
Conversion Efficiency (%)	70.2	82.7	59.6	64.2	74.7	90.0	90.0	90.0
Unit Capital Cost $\frac{\$}{\text{kW(th)}}$	-	-	-	-	320	150	150	150
<u>Basic Fuel Cost</u>								
Year 1985 (\$/M Btu)	2.15	2.52	0.74	0.74	0.76	0.76	0.76	2.53
Year 2000 (\$/M Btu)	2.41	3.15	0.82	0.82	0.88	0.88	0.88	2.65
<u>Unit Production Costs - 1985</u>								
Capital Cost (7) (\$/M Btu)	0.65	1.64	2.54	2.06	5.50	2.58	0.94	1.31
Fuel Cost (\$/M Btu)	3.06	3.05	1.24	1.15	3.08	2.56	2.56	8.53
O and M Cost (6) (\$/M Btu)	0.50	0.50	1.34	1.25	0.47	0.47	0.47	0.47
<u>Total Unit Cost (\$/M Btu)</u>	4.21	5.19	5.12	4.46	9.05	5.61	3.97	10.31
<u>Unit Production Costs - 2000</u>								
Capital Cost (7) (\$/M Btu)	0.65	1.64	2.54	2.06	5.50	2.58	0.94	1.31
Fuel Cost (\$/M Btu)	3.43	3.81	1.38	1.28	3.46	2.88	2.88	8.66
O and M Cost (6) (\$/M Btu)	0.50	0.50	1.34	1.25	0.47	0.47	0.47	0.47
<u>Total Unit Cost (\$/M Btu)</u>	4.58	5.95	5.26	4.59	9.43	5.93	4.29	10.44

Footnotes for Table 5.1

1. Plant capacity, capital cost, conversion efficiency and annual load factor are from the Exxon study [11]. The investment cost figures are converted from 1980 to 1975 dollars using a nine percent annual discount factor, based on a private communication from H. G. Corneil (Exxon Research and Engineering Company) to C. Braun, BNL, November 15, 1976.
2. Lurgi Electrolyzer capacity, capital cost and conversion efficiency data obtained from the EPRI/IGT report on Utilization of Off-Peak Electric Power [12], Table III-1 and III-2.
3. Plant capacity, capital cost and conversion efficiency of solid-polymer-electrolyte, water-electrolysis equipment based on communication from R. Fernandes (Niagara Mohawk Power Corp.) to the Ad Hoc Committee on Hydrogen as a Natural Gas Supplement, November 12, 1976 [13].
4. Electricity supplied to the water electrolysis plant is assumed to be provided by a LWR nuclear power plant having the following economic parameters:
 - (a) Capital cost of \$585/kW(e) in 1974 dollars [14], escalated to 1975 dollars assuming 5%/year escalation rate according to [15].
 - (b) Nuclear fuel cycle cost - \$0.65/M Btu and \$0.77/M Btu in 1985 and 2000, respectively, according to [14].
 - (c) Operating and maintenance costs of 1.2 mills/kWh according to [14], or the equivalent of \$0.11/M Btu.
 - (d) Thermal efficiency of 0.33 and 0.34 in 1985 and 2000, respectively, according to [14].

- (e) Base-load, annual-average load factor of 0.65 according to [14].

Spinning reserve is assumed available on a year-round basis (7920 hr/year) at nuclear-fuel price. Off-peak and spinning-reserve operation are charged only the variable, i.e., fuel and O and M nuclear costs which amount to 7.86 and 9.10 (mills/kWh) in 1985 and 2000, respectively. The water electrolysis plant operated in conjunction with a dedicated nuclear plant is charged the full nuclear electricity cost which amounts to 26.2 and 27.1 (mills/kWh) in the years 1985 and 2000, respectively.

5. Fossil fuels costs, including raw fuel cost and incremental fuel processing expenses were obtained from [14].
6. Operating and maintenance costs of fossil-fuel-based hydrogen production plants were obtained from [14]. Water-electrolysis plants O and M costs were obtained from [13].
7. Annual fixed charges on capital are assumed at 17% of investment per year according to [16].

Area 5: Hydrogen Storage Systems Analysis

References

- [1] C. Braun, E. A. Cherniavsky, F. J. Salzano, The economic incentive for introducing electric storage devices into the national energy system, Proc. 10th Intersociety Energy Conv. Eng. Conf., Newark, Delaware, September 1975, (BNL 20450).
- [2] C. Braun, E. A. Cherniavsky, F. J. Salzano, The Role and Allowed Costs of Fuel Cells as Electric Generating Devices, September 1975, Informal Report (BNL 20504).
- [3] C. Braun, E. A. Cherniavsky, F. J. Salzano, The target capital costs for the implementation of fuel cells and electric storage devices within the national energy system, Proc. 148th Meeting of the Electrochemical Society, Dallas, Texas, October 1975, (BNL 20523).
- [4] C. Braun, E. A. Cherniavsky, F. J. Salzano, The integration of distillate oil/hydrogen fueled fuel cells into the national energy system, Proc. 1st World Hydrogen Energy Conference, Miami Beach, Florida, March 1976, (BNL 20989).
- [5] C. Braun, Memorandum to F. J. Salzano regarding Impact Analysis for Enthalpy Management in Building Systems, September 1975, (BNL 20524).
- [6] U.S. ERDA, Creating Energy Choices for the Future. A National Plan for Energy Research, Development and Demonstration, Washington, D.C., July 1975.
- [7] F. J. Salzano, C. Braun, Water electrolysis vs. thermochemical production of hydrogen: a parametric assessment, Proc. 1st World Hydrogen Energy Conference, Miami Beach, Florida, March 1976, (BNL 20878).
- [8] F. J. Salzano, E. Gileadi, S. Srinivasan, C. Braun, A. Beaufriere, S. Gottesfeld, An electrochemically regenerative hydrogen-chlorine energy storage system for electric utilities, Proc. 11th Intersociety Energy Conversion Engineering Conference, Nevada, September 1976, (BNL 21820).
- [9] C. Braun, F. J. Salzano, The Economics of Hydrogen Enrichment of Natural Gas - A Preliminary Assessment, Draft Report, April 1976.

- [10] F. J. Salzano, C. Braun, Editors, Hydrogen Energy Assessment, A preliminary report prepared by Brookhaven National Laboratory for the Office of the Assistant Administrator for Planning and Analysis, U.S. ERDA, November 1976.
- [11] H. G. Corneil, F. J. Heinzelmann, E. W. Nicholson, Production Economics for Hydrogen, Ammonia, and Methanol During the 1980-2000 Period, report prepared by Exxon Research and Engineering Company for Brookhaven National Laboratory, September 1976, (BNL 50663).
- [12] N. Biederman, K. Darrow, Jr., A. Konopka, Utilization of Off-Peak Power to Produce Industrial Hydrogen, Electric Power Research Institute, final report on Research Project 320-1, Palo Alto, California, August 1975.
- [13] R. Fernandes, (Niagara Mohawk Power Corp.), Draft Summary Report of the Supply Task Group Communication to Members of the Ad Hoc Committee on Hydrogen as a Natural Gas Supplement, Syracuse, New York, November 12, 1976.
- [14] U.S. ERDA - Office of the Assistant Administrator for Planning Analysis and Evaluation. Working Paper Forecasts and Scenarios 1985-2000 (revised draft), September 10, 1976.
- [15] U.S. ERDA - Office of the Assistant Administrator for Planning Analysis and Evaluation. Briefing for Assistant Administrator's Presentation of ERDA Electric Utilities Study (revised), Washington, D.C., May 26, 1976.
- [16] Economic Evaluation Sub-Task Group - Ad Hoc Committee on Hydrogen as a Natural Gas Supplement, Sample Hydrogen Production Cost Analysis included in the Minutes of the Fourth Meeting of the Ad Hoc Committee held in Chicago, Illinois, September 1976. Minutes distributed by BNL on November 15, 1976.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

AREA 6: PROJECT MANAGEMENT

BNL fully assumed its role in Hydrogen Project Management under the direction of the Energy Storage Systems Division of ERDA. The ERDA Headquarters Division provides guidance in policy matters and program goals; and the ERDA Area Office at Brookhaven, in coordination with the Chicago Operations Office, provide support in program execution, contracts, and procedural matters.

A dedicated Conservation Program Management Group (CPMG) was established within BNL and its responsibilities were defined and endorsed by the Laboratory management. The CPMG has been staffed and its operating procedures and relationships with the ERDA offices are developed and are being implemented. The BNL Project Management tasks outlined in the ERDA authorization letter for the hydrogen program were performed, and the accomplishments in the four major areas of responsibility were as follows.

6.1 Planning and Analysis

The BNL Project Management Group assisted ERDA in preparing the FY 1977 PAD document defining program plans, schedules, and resource allocations. BNL participated in a number of budget exercises to provide detail and support ERDA in defining funding priorities. The project plan (mini-pad) developed was patterned after the ERDA STOR PAD to provide detail on the goals, objectives, and content of specific technical areas. Milestone schedules were prepared with various levels of detail to be used for identification and control of critical points in the project.

Within BNL, the Schedule 189 proposal for the hydrogen project was prepared and serves as the contractual and operating document for the project.

Procedures were set up to obtain current budget information for both the internal BNL work and the subcontracted or monitored activities in order to provide control on spending rates. All of the above information is maintained current in a separate management action/planning center established at BNL for this purpose. The information was used on many occasions to support either ERDA or BNL management reviews.

6.2 Contract Management

During the course of the year, the BNL CPMG has managed or monitored over 20 technical research and development contracts whose face value is over \$1 million. This responsibility included preparation of contract documents, and preparation of progress reports, including budget and spending-rate information. In addition, it included addressing issues such as patent rights, proprietary material and carry-over budget authority, and defining and implementing the BNL/ERDA position as applicable. Contractors managed during 1976 included GE, Exxon, Teledyne, PSE&G, University of Virginia, and others.

A second task in contract management consisted of coordinating the evaluation of over 30 unsolicited proposals submitted to either BNL or ERDA. This included obtaining independent reviews, holding evaluation committee meetings, and documenting the decisions of the committee. These proposals were submitted by large industrial firms, universities, organizations, companies located in foreign countries, and individuals.

A third area of work was the preparation and processing of RFP's of which three are planned for release in FY 1977 covering light-weight hydrogen storage materials, underground storage, and hydrogen-storage systems studies. The processing includes publicizing the RFP, handling the responses, making the evaluation, and selecting the winning proposal.

In addition to the above, a separate task of technical monitoring was performed on all contracts, both BNL-originated and where the contractual document was issued from an ERDA operations office. This effort involved evaluating progress, inspecting research units and facilities, attending review meetings, and recommending corrective action to ERDA. This activity was performed on contracts with University of Georgia, Stevens Institute, General Electric, PSE&G, and others.

6.3 Technical Management

As part of the project technical management activities, a second Hydrogen Contractor's Review Meeting was planned and coordinated by BNL and held at Airlie, Virginia in November 1976. It involved all aspects of the chemical storage-hydrogen program with over 30 papers presented and approximately 75 participants. The proceedings of the meeting were subsequently published by ERDA [1].

The technical management task also included preparing and/or reviewing the technical input to documents such as RFP's, contracts or information publications for the technical areas in the hydrogen project over which BNL has cognizance. Related to this effort was the work done in supporting congressional inquiries with technical expertise for questions originating from constituents or special interest groups.

6.4 Liaison Activities

A separate activity in project management is the liaison and coordination of the work being done in hydrogen systems by various government agencies, national laboratories, private industry, universities, and individuals. The purpose of this activity is to aid in the implementation and commercialization of hydrogen technology and to address the institutional problems involved. To this end a number of activities were performed,

including the following: (1) Coordinating the Ad Hoc Advisory Committee on Natural Gas Supplementation involving over forty electric and gas utilities representatives; (2) conducting Hydrogen Contractors' Review Meeting; (3) participation in International Energy Agency activities; (4) visits and discussions at the request of foreign countries (Brazil, European Community) to develop working agreements in hydrogen research and development; and (5) participation in meetings, workshops, etc., sponsored by the American Gas Association (AGA), Electric Power Research Institute (EPRI), and other similar organizations.

A BNL Liaison Office was opened in Washington, D.C., in October 1976. This office, which has a small full-time staff, provides liaison with ERDA Headquarters in connection with BNL programs for the Division of Energy Storage Systems and the Division of Buildings and Community Systems. The location of the office provides close coordination not only with ERDA but with the other national laboratories having similar offices in the same building.

Area 6: Project Management

References

- [1] U.S. ERDA, Proceedings of the ERDA Contractors' Review Meeting on Chemical Energy Storage & Hydrogen Energy Systems, Airlie House, Airlie, Virginia, November 8-9, 1976. (Conf-761134)

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

APPENDIX A

Figure 3A1: Pressure-composition desorption isotherms for the $\text{TiFe}_{0.6}\text{Mn}_{0.2}\text{-H}$ system at several temperatures.

Figure 3A2: Hysteresis in the $\text{TiFe}_{0.6}\text{Mn}_{0.2}\text{-H}$ system at 30°C .

Figure 3A3: Pressure-composition desorption isotherms for the $TiFe_{0.6}Mn_{0.3}$ -H system at several temperatures.

Figure 3A4: Hysteresis in the $\text{TiFe}_{0.6}\text{Mn}_{0.3}\text{-H}$ system at 30°C .

Figure 3A5: Pressure-composition desorption isotherms for the $TiFe_{0.5}Mn_{0.3}$ -H system at several temperatures.

Figure 3A6: Hysteresis in the $TiFe_{0.5}Mn_{0.3}-H$ system at $30^\circ C$.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

Figure 3A8: Pressure-composition desorption isotherms for the $\text{TiFe}_{0.7}\text{Mn}_{0.18}\text{-H}$ system (INCO-1) at several temperatures.

Figure 3A9: Hysteresis in the $\text{TiFe}_{0.7}\text{Mn}_{0.18}\text{-H}$ system (INCO-1) at 30°C .