350
2-19-80

DR. 858

SAN-1485-T1

HIGH-TEMPERATURE FUEL CELL RESEARCH AND DEVELOPMENT

Annual Technical Status Report, October 1, 1978–September 30, 1979

MASTER

Work Performed Under Contract No. EC-77-C-03-1485

Montana Energy and MHD Research and Development Institute, Inc.
Butte, Montana

U. S. DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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.

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.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$4.00
Microfiche \$3.00

ANNUAL
TECHNICAL STATUS REPORT

DISCLAIMER

This book 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.

Period Covered: October 1, 1978 - September 30, 1979
(Work Period Covered: March 1, 1979 - September 30, 1979)

HIGH-TEMPERATURE FUEL CELL RESEARCH AND DEVELOPMENT

Contract No. DE-AC03-77-ET-11320

Prepared by
Montana Energy and MHD Research and
Development Institute, Inc.,
Butte, Montana

Submitted to
U. S. Department of Energy
Office of Fossil Energy

Division of Power Systems DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

HIGH-TEMPERATURE FUEL CELL RESEARCH AND DEVELOPMENT

I. OBJECTIVE

The object of this program is to develop strong thin fibers of materials which are chemically and physically stable in molten carbonate fuel cell electrolyte at 600 to 700°C and to perform the materials characterization necessary to determine the stability of the fibers in the molten carbonate electrolyte.

II. CONTRACT BACKGROUND

This work is a continuation of Contract No. EC-77-C-03-1485. A proposal for renewal of the work for FY 79 was submitted to DOE 29 June 1978, revised and expanded work statements were mailed to a DOE representative (Mr. Richard Dudley) on 1 August 1978. Advance agreements were obtained to cover costs charged after October 30, 1978. These costs included subcontract work performed in FY '78 and attendance at a Fuel Cell Workshop, October 31, 1978. Actual work charged under the precontract agreement did not begin until March 1979. Work was somewhat inhibited by the absence of negotiated work statements. After contract negotiation MERDI representatives signed the contract 19 July 1979 and received the DOE signed contract 1 August 1979. The original proposal was for two tasks, molten carbonate task and a solid electrolyte task. No funds were allotted for solid electrolyte work. The extended contract is to run until February 1979.

III. PROGRESS SUMMARY

The signing of the renewal contract established a Statement of Work. From the Statement of Work we (MERDI) abstracted tasks and subtasks. The two tasks are: 1) Identify Materials and 2) Fiber Preparation.

Subtasks were identified as:

- 1.1 List Candidate Materials
- 1.2 Determine Chemical Stability of Candidate Materials,
- 1.3 Determine Physical Stability of Candidate Materials,
- 2.1 Prepare Fibers, and
- 2.2 Evaluate Fibers.

A project Milestone Chart was established by MERDI that showed tasks, subtasks, tests used in support of subtasks, information due in reports and a tentative timetable. The timetable was established as a guideline for the tasks that would correspond to a completion of all tasks by 28 February 1980. It was recognized (due to problems of delays, funding cuts, and restriction on capital equipment) that it might not be possible to meet the time schedule outlined in the Milestone Chart. However, concerted effort is being made to meet that schedule with the understanding that a no-cost extension might be required starting March 1, 1980.

A copy of the MERDI Milestone Chart is included with this report. Progress is illustrated by filling in the horizontal bars as tasks are accomplished. The chart is correct for the date of this report.

Task 1 - Materials Identification

The final list of ceramic candidates was established and hereby is being reported as:

- 1) Al rich MgAl_2O_4 ,
- 2) ThO_2 ,
- 3) ZrO_2 stabilized with Y+Cr,
- 4) ZrO_2 stabilized with Ca,
- 5) Al_2O_3 doped with 20 mole % Cr,
- 6) Mg rich MgAl_2O_4 ,
- 7) MgZrO_3 ,
- 8) CaZrO_3 ,
- 9) Y_2O_3 : Al_2O_3 ,
- 10) MgTa_2O_6 ,
- 11) Cobalt Aluminate-- CoAl_2O_4 ,
- 12) $\gamma\text{-LiAlO}_2$ (for reference).

Candidates No's 1, 3, 5, 6 were fabricated at MERDI and the remainder purchased from commercial sources. The list of candidate materials was formulated based both on results of crucible corrosion tests in FY 78 (many materials were found unsatisfactory and are listed in the Final FY 78 Report) and the topical report "Evaluation of MHD Materials for Use in High-Temperature Fuel Cells," by Ronald Guidotti of MERDI dated 15 June 1978.

All candidate materials were characterized prior to corrosion testing utilizing a) Chemical Analysis, b) X-ray Diffraction For Phase Identification, c) Scanning Electron Microscopy, d) B.E.T. surface area analysis. Extremely careful and detailed testing was performed in every case in order to provide an accurate baseline with which to compare the ceramics after corrosion testing. If detailed chemical analysis was not available on starting materials, emission spectro chemical analysis was performed. Only a portion of the chemical analysis information on hand is reported in Table I. The x-ray diffraction work was performed using unfiltered Cu radiation in order to increase the intensity of any minority phases present. This leads to the presence of K_{β} peaks in the patterns and, for many of the ceramic compositions, complicated (many peaks) patterns result. In order to enhance analysis and use quantitative match parameters, we are using a computer program written for JCPDS called the Johnson Search Match program. All compositions have been x-rayed prior to testing but the results haven't all been processed on the computer, hence the designation of "I.P." or "Result Analysis in Process" entries in Table I. Both the surface area and x-ray diffraction for ThO_2 in Table I are not available. We are relying on the SEM results alone to define the ThO_2 morphology. The B.E.T. and x-ray testing is performed out of house and the instruments are not contained in a hood for proper handling of the alpha emitting ThO_2 .

Extensive work was performed in characterizing the powders using SEM micrographs. Results were quantified by counting up to 500 particles using random linear intercept techniques. Normally both an agglomerate size and range were determined. The morphology was also noted. The agglomerate is a collection of individually discernable particles that

are "stuck" together either by sintering or other bonding. The bonding ranges from very strong to fairly light. An examination of typical SEM micrographs (Figures 1-a through 11-b) show the great variety in agglomerates and morphology encountered in this study. This information can be used in conjunction with the macroscopic surface area and mesh information to form a more complete characterization of powders--both prior and post testing.

A partial summary of properties prior to corrosion testing is given in Table I.

A fuel gas atmosphere to be used as a cover gas in the corrosion experiments was selected and submitted to Mr. R. Dudley, 30 March 1979. The composition is based on reformed Naptha at an operating temperature of 700°C and is:

50.2% H_2

10.8% CO

9.5% CO_2

29.5% H_2O

The use of a fuel gas atmosphere necessitated the modification and addition of flow meters, bubblers, heaters and circulators, etc. to our gas supply and disposal trains. Necessary components were ordered, delivered, system built and are currently installed on three corrosion test furnaces.

Alumina crucibles were evaporatively and then electrolytically coated with gold (99.99% pure) to a thickness of approximately 0.002" with good results. These crucibles are then used as an inert container for the mixed carbonates and the candidate ceramic powder during the high temperature (700°C) testing.

20x

2000x

Figure 1-a.--Al rich MgAl_2O_4

5000x

Figure 1-b.--Al rich MgAl_2O_4

250x

Figure 2-a.--ThO₂

2500x

Figure 2-b.--ThO₂

100x

500x

Figure 3-a.-- $\text{ZrO}_2 + \text{Y} + \text{Cr}$

1500x

Figure 3-b.-- $\text{ZrO}_2 + \text{Y} + \text{Cr}$

1000x

Figure 4-a.--ZrO₂ stabilized with Ca

3000x

Figure 4-b.--ZrO₂ stabilized with Ca

Figure 5-a.--Mg rich MgAl_2O_4

10,000x

Figure 5-b.--Mg rich MgAl_2O_4

200x

1000x

Figure 6-a.-- MgZrO_3

Figure 6-b.-- MgZrO_3

200x

1000x

Figure 7-a.--CaZrO₃

3000x

Figure 7-b.--CaZrO₃

200x

1000x

Figure 8-a.-- $\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$

200x

Figure 8-b.-- MgTa_2O_6

1000x

5000x

Figure 9-a.-- MgTa_2O_6

10,000x

Figure 9-b.-- MgTa_2O_6

1000x

Figure 10-a.--CoAlO₄

300x

1500x

Figure 10-b.--Unground α -LiAlO₂

200x

2000x

Figure 11-a.--Ground γ -LiAlO₂

50x

Figure 11-b.--1350°C Fired γ -LiAlO₂ fibers

TABLE I.--Properties of Candidate Materials Prior to Testing

Material	Avg. Particle Size	Surface Area	Mesh	Purity (%)	PDF #	Source
Al rich $MgAl_2O_4$	100 μ mean agglomerate 0.7 μ mean particle	I.P.	-100	99.7	21-1152 -Spinel negligible $\alpha-Al_2O_3$	MERDI made from reagent grade materials via isopropoxide technique. 45 MgO-55 Al_2O_3
TiO_2	100 μ mean agglomerate 0.4 μ mean particle	N.A.	-100	Nat. Occurring 99.9%	N.A.	RIC/ROC PH10
ZrO stabilized with Y_2O_3 and Cr_2O_3	4 μ m mean particle (0.01- 10 μ range)	I.P.	-325	99.9% (Zr .785 Hf .015 Cr .10 Y .10 O_2)	I.P.	MERDI made from: 'Magnesium Electron Co' S grade ZrO_2 'Moly Corp' 99.99% Y_2O_3 'J. T. Baker' C.P. grade Cr_2O_3
ZrO ₂ stabilized with CaO	2.3 μ mean particle (0.1-6 μ range) (50% finer than 4 microns)	1.15 $\frac{m^2}{g}$	-325	91.5 % ZrO_2 2.0 % HfO_2 5.0 % CaO .6 % SiO_2 .4 % MgO .2 % Al_2O_3 .15% Fe_2O_3 .15% TiO_2	24-1074 cubic	Zirconium Corp. of America Zircoa-B

I.P. = Results Analysis in Process
N.A. = Not Available

TABLE I.--Properties of Candidate Materials Prior to Testing

Material	Avg. Particle Size	Surface Area	Mesh	Purity (%)	PDF #	Source
$\text{Al}_2\text{O}_3 + 20 \text{ mol } \% \text{Cr}_2\text{O}_3$	0.4 μ mean particle	I.P.	-150	($\text{Al}_{1.8}\text{Cr}_{0.2}$) $_2\text{O}_3$ 99.9% 0.023 % MgO	Dist. 10-173 Distorted $\alpha\text{-Al}_2\text{O}_3$	MERDI made from 'Reynolds RC-HP-DBM' Al_2O_3 'J. T. Baker Analyzed Reagent' $\text{Cr}(\text{NO}_3)_3$
Mg rich MgAl_2O_4	300 μ mean agglomerate (10-500 μ range) 0.4 μ mean particle (0.1 - 1 μ range)	I.P.	-60	99.3%	MgO - 4-829 + Spinel - 21-1152	'Dead Sea Periclase' Gem 995 MgO 'Reynolds RC-HP-DBM' Al_2O_3 65 MgO - 35 Al_2O_3 MERDI made
-17- MgZrO_3	8 μ mean agglomerate (3-50 μ range) 4 μ mean particle (0.6- 6 μ range)	6.5 m^2/g	-325	98.0% SiO_2 0.8% LOI 1.0%	I.P.	'Zirconium Corp of America 05-0295-401'
CaZrO_3	2.3 μ mean particle (0.1- 6 μ range)	4.0 m^2/g	-325	98.0% SiO_2 0.8% LOI 1.0%	9-364 orthorhombic	'Zirconium Corp of America 05-0268-215'
$\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$	5 μ mean particle	4.3 m^2/g	-150	99.9%	I.P.	Atomergic Chemetals
MgTa_2O_6	30 μ mean spherical agglomerates 90 μ mean length ta- bular agglomerates 15 μ mean width tabular agglomerates 4 μ mean thickness ta- bular agglomerates 0.07 μ mean particle size (0.01 - 2 μ range)	1.1 m^2/g	-150	99.9%	14-680 tetragonal Trace MgO 4-829	'Cerac Inc. M-1025 Lot 8095-A-Z'

I.P. = Result Analysis in Process

N.A. = Not Available

TABLE I.--Properties of Candidate Materials Prior to Testing

<u>Material</u>	<u>Avg. Particle Size</u>	<u>Surface Area</u>	<u>Mesh</u>	<u>Purity (5)</u>	<u>PDF #</u>	<u>Source</u>
Cobalt Aluminate (CoAl_2O_4)	40 μ mean agglomerate (20-100 μ range) 10 μ mean particle (2-30 μ range)	10.8 m ² /g	-100	98.0 %	I.P.	ROC/RIC Sun Valley, Calif. CO-58
γ - LiAlO_2	<u>Unground</u> 200 μ mean agglomerate (100-300 μ range) 15 μ mean particle (5-50 μ range) <u>Ground</u> 0.10 μ mean particle	I.P.	-400	Li_2O 21.4 % purified grade	18-714	Alpha Ventron - #11119 ROC/RIC Li-58
			-425			

I.P = Results Analysis in Process
N.A.= Not Available.

As shown in the Milestone Chart all 200 hour corrosion tests are now complete. The post 200 hour exams for corrosion and physical stability are still in progress. These tests include: 1) X-ray diffraction to determine phase stability (we now have a workable computer search/match capability), 2) Atomic Absorption Analysis (AA) of leached carbonate to determine solubility of ceramic in molten carbonate, 3) SEM determination of morphology and profile size change, and 4) Surface Area Change in tested powders (reliability and precision of this B.E.T measurement may preclude extensive use of this technique).

A subcontract for fiber strength measurements was executed with Dr. Richard Tressler of Pennsylvania State University with an 1 August 1979 starting date and a 31 January 1980 ending date. Samples of Al_2O_3 fibers packaged by various attachment techniques were sent to Dr. Tressler for evaluation and recommendation of forming, firing and shipping technique for maximum strength and ease of handling. The best shipping technique found was to glue the ends of the fibers to a card and place the card slightly curved in a plastic tube. Upon his initial recommendations more fibers were fabricated and sent to Dr. Tressler. Initial strength testing revealed interesting modulus properties but testing is still in its early stages.

Task 2 - Fiber Formation

Formulation of a batch composition for gamma $LiAlO_2$ was completed using commercial gamma $LiAlO_2$. The resulting slurry was formed into green fibers and then sintered at temperatures including 1100°C and 1350°C. Sintering at 1100°C in air resulted in fibers of little strength; fibers fired at 1350°C in air gave better strength results. Temperatures are to be kept less than 1450°C because of anticipated lithium losses and phase changes. Fibers are currently being evaluated by SEM and x-ray diffraction. Diffraction results indicate a small change in the patterns after sintering at 1350°C. These results are being analyzed carefully using our search/match computer program. If phase changes are evident a new firing schedule or alternate firing techniques are being considered.

IV. PROBLEMS

None

V. CONCLUSIONS

None

HIGH TEMPERATURE FUEL CELL RESEARCH AND DEVELOPMENT	

YEAR	1979	1980
MONTH	M A M J J A S O N D J F	

-21-

PROJECT MILESTONE CHART

HIGH TEMPERATURE FUEL CELL RESEARCH AND DEVELOPMENT

TASK 1. IDENTIFY MATERIALS
REPORT DUE ○

YEAR
MONTH

1979

1980

M A M J J A S O N D J F

MAJOR MILESTONES AND
DECISION POINTS

1.3 DETERMINE PHYSICAL STABILITY OF
CANDIDATE MATERIALS

- . POST 200 HOUR EXAM (TEN)
- . S.E.M.
- . B.E.T.
- . 1000 HOUR TESTS (?)
- . POST 1000 HOUR EXAM.
- . S.E.M.
- . B.E.T.
- . X-RAY DIFFRACTION

PROJECT MILESTONE CHART

HIGH-TEMPERATURE FUEL CELL RESEARCH AND DEVELOPMENT

TASK 2. FIBER PREPARATION!
REPORT DUE ○