15:55:12 OCA PAD AMENDMENT - PROJECT HEADER INFORMATION 07/12/94

Active

Project #: E-19-683 Cost share #: Rev #: 6
Center # : 10/24-6-R7311-0A0 Center shr #: OCA file #:
Work type : RES
Contract#: DE-FG22-91PC91288 Mod #: M004 Document : GRANT
Prime #: Contract entity: GTRC

Subprojects ? : N CFDA: 81.049
Main project #: PE #: N/A

Project unit: CHEM ENGR Unit code: 02.010.114
Project director(s):
WINNICK J CHEM ENGR (404)894-2839

Sponsor/division names: US DEPT OF ENERGY / DOE PITTSBURGH - PA
Sponsor/division codes: 141 / 005

Award period: 910901 to 941231 (performance) 950331 (reports)

Sponsor amount	New this change	Total to date
Contract value	0.00	199,977.00
Funded	0.00	199,977.00
Cost sharing amount		0.00

Does subcontracting plan apply ?: N

Title: HIGH TEMPERATURE ELECTROCHEMICAL SEPARATION OF H2S FROM COAL GASIFICATION

PROJECT ADMINISTRATION DATA

OCA contact: E. Faith Gleason 894-4820

Sponsor technical contact

KAMALENDU DAS
(304)291-4065

U.S. DEPT. OF ENERGY
MORGANTOWN ENERGY TECHNOLOGY CENTER
P.O. BOX 880
3610 COLLINS FERRY ROAD
MORGANTOWN, WEST VIRGINIA 26507-0880

Sponsor issuing office

JO ANN C. ZYSK
(412)892-6200

U.S. DEPT. OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
P.O. BOX 10940, MS 921-118
PITTSBURGH, PA 15236-0940

Security class (U,C,S,TS) : U ONR resident rep. is ACO (Y/N): N
Defense priority rating : N/A DOE supplemental sheet
Equipment title vests with: Sponsor GIT X

Administrative comments -
AMENDMENT #M004 PROVIDES A NO-COST EXTENSION TO DECEMBER 31, 1994.

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 04/04/95

Project No. E-19-683 Center No. 10/24-6-R7311-0A0

Project Director WINNICK J School/Lab CHEM ENGR

Sponsor US DEPT OF ENERGY/DOE PITTSBURGH - PA

Contract/Grant No. DE-FG22-91PC91288 Contract Entity GTRC

Prime Contract No. _____

Title HIGH TEMPERATURE ELECTROCHEMICAL SEPARATION OF H2S FROM COAL GASIFICATION

Effective Completion Date 941231 (Performance) 950331 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	
Final Report of Inventions and/or Subcontracts	Y	
Government Property Inventory & Related Certifica+	Y	950202
Classified Material Certificate	N	
Release and Assignment	N	
Other _____	N	

Comments_____
NOTE: USE DOE FORM FOR PATENT_____

Subproject Under Main Project No. _____

Continues Project No. _____

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

NOTE: Final Patent Questionnaire sent to PDPI.

DOE F538 (5-86)

OMB Control No. 1910-1400

U. S. DEPARTMENT OF ENERGY

NOTICE OF ENERGY RD&D PROJECT

1. Descriptive TITLE of work (150 characters including spaces)

High Temperature Electrochemical Separation of H_2S from Coal Gasification Process Streams

2. CONTRACT or grant number DE-FG22-91PC91288

2A. MASTER contract number (GOCO's)

2B. Responsible PATENT office Pittsburgh, PA

3. Performing organization CONTROL number (internal) E-19-683

3A. Budget and Reporting code

3B. Funding YEAR for this award 1991

4. Original contract start date 090191

4A. Current contract start date 090191

4B. Current contract close date 090194

4C. Anticipated project termination date 090194

5. Work STATUS

☐ Proposed ☐ Renewal

XXX New ☐ Terminated

5A. Manpower (FTE)

5B. CONGRESSIONAL district 5th

5C. STATE or Country where work is being performed Georgia

5D. COUNTRY sponsoring research

6. Name of PERFORMING organization Georgia Tech Research Corporation
Georgia Institute of Technology, School of Chemical Engineering

6A. DEPARTMENT or DIVISION	6B. Street Address	6C. City, State, Zip Code
School of Chemical Engineering	Georgia Institute of Technology	Atlanta, GA 30332-0100

7. Circle only one code for TYPE of Organization Performing R&D:

CU - College, university, or trade school
FF - Federally funded RD&D centers or laboratory operated for an agency of the U. S. Government
IN - Private industry
NP - Foundation or laboratory not operated for profit
ST - Regional, state or local government facility
TA - Trade or professional organization
US - Federal agency
XX - Other
EG - Electric or gas utility

8A. Contractor's PRINCIPAL INVESTIGATOR/s or project manager Name/s (Last, First, MI) Winnick, Jack

8B. PHONE/s (in order of PI names with commercial followed by FTS)

Comm. 404/894-2839 ; FTS ; Comm. ; FTS

8C. PI/s address (if different from that of Performing Organization)

9. DOE SUPPORTING Organization (DOE Assistant Secretary and office sponsoring the work; technical monitor; and administrative monitor).

9A. PROGRAM division or office (full name) Pittsburgh Energy Technology Center

Program Office Code

9B. TECHNICAL monitor (Last, First, MI)

9C. Address

9D. Phone Comm.

FTS

9E. ADMINISTRATIVE monitor (Last, First, MI)

10. FUNDING in thousands of dollars (K$). Funds represent budget obligations for operating and capital equipment (FY runs October 1 – September 30).

Funding organization(s)	Current FY 1991	Next FY 1992
A. DOE	69	48
B.		
C.		

10D. Does the current FUNDING cover more than one year's work? Yes XX No

E. If yes, provide dates (from when to when). 090191 to 090194

11. Descriptive SUMMARY of work. Enter a Project Summary using complete sentences limited to 200 words covering the following: Objective(s), state project objectives quantifying where possible (e.g., "The project objective is to demonstrate 95% recovery of sulfur from raw gas with molten salt recycling at a rate of one gallon per minute."); approach, describe the technical approach used (how the work is to be done); expected product/results, describe the final products or results expected from the project and their importance and relevance.

An advanced process for the separation of hydrogen sulfide from coal gasification streams through an electrochemical membrane will be developed. H_2S is removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. The process allows removal of H_2S without cooling the gas stream and with negligible pressure loss through the separator. The process is economically attractive by the lack of absorbents and the lack of a Claus process for sulfur recovery.

12. PUBLICATIONS available to the public. List the five most descriptive publications that have resulted from this project in the last year that are available to the public. (Include author, title, where published, year of publication, and any other information you have to complete full bibliographic citation.) Use the back of this form or additional sheets if necessary.

13. KEYWORDS (Listed five terms describing the technical aspects of the project. List specific chemicals and CAS number, if applicable.)

membranes, gas separation, hot-gas desulfurization, electrochemical processing, ceramic membrane preparation

14. RESPONDENT. Name and address of person filling out the Form 538. Give telephone number, including extension (if you have FTS number, please include it) at which person can be reached. Record the date this form was completed or updated. The information in Item 14 will not be published.

Respondent's Name: Professor Jack Winnick Phone No.: 404/894-2839 Date: Sept. 23, 1991

Street: Georgia Institute of Technology

City: Atlanta State: GA Zip: 30332-0100

GEORGIA TECH RESEARCH CORPORATION

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
PROGRAM ADMINISTRATION DIVISION
ATLANTA, GEORGIA 30332-0420
USA

Telex: 542507 GTRC OCA ATL
Fax: (404) 894-5945

Phone: (404) 894-4820

February 9, 1993

Document Control Center
US Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940, MS 921-118
Pittsburgh, PA 15236-0940

SUBJECT: Grant No. DE-FG22-91PC91288, Notice of Energy RD&D

Enclosed is the Notice of Energy RD&D for the period ending August 31, 1992 submitted in accordance with the US Department of Energy Federal Assistance Reporting Checklist.

Should you have any questions or need additional information, please do not hesitate to contact me at (404) 894-4820.

Sincerely,

E. Faith Gleason
Contracting Officer

Enclosure: 3 Copies

xc: Jo Ann Zysk

FILE
Rpts. Coord.

DOE F 1430.22
(04-91)
All other editions
are obsolete
(Replaces DOE F 538)

OMB Control No.
1910-1400
Burden Disclosure
Statement on Back

U.S. DEPARTMENT OF ENERGY
NOTICE OF ENERGY RD&D PROJECT

1. DOE CONTRACT OR GRANT NUMBER DE-FG22-91PC91288

   ☐ New contract ☒ Continuation/Revision

2. A. NAME OF PERFORMING ORGANIZATION Georgia Tech Research Corporation

   B. Department or Division School of Chemical Engineering

   C. Street Address Bunger Henry Building

   City Atlanta State Georgia Zip 30332-0100

   D. Type of Performing Organization (circle only one two-letter code)

   CU–College, university, or trade school
   EG–Electric or gas utility
   FF–Federally funded RD&D centers or laboratory operated for agency of US government
   IN–Private industry
   NP–Foundation or laboratory not operated for profit
   ST–Regional, state, or local government facility
   TA–Trade or professional organization
   US–Federal Agency
   XX–Other

3. PRINCIPAL OR SENIOR INVESTIGATOR

   A. Last Winnick First Jack MI

   B. Phone: Commercial (404) 894-2839 FTS

4. DOE SPONSORING OFFICE OR DIVISION Pittsburgh Energy & Technology Center

5. TITLE OF PROJECT High Temperature Electrochemical Separation of H2S from Coal Gasification Process Streams.

6. DESCRIPTIVE SUMMARY (limit to 200 words)

Selective removal of H_2S from coal gas streams by a high temperature (650° C) electrochemical operation is being perfected. The operation, which takes advantage of an electrochemical potential gradient rather than conventional techniques, removes H_2S from the coal gas stream, leaving H_2 to enrich the exiting gases. Sulfur is the by-product which is swept away by an inert sweep gas and condensed downstream.

Current experiments are based on improving selective removal from low initial H_2S concentrations (10 ppm). High flow rate effects, membrane stability & selectivity, and cell housing seals characterize present studies, although recent results already show over 90% removal with applied current.

7. RESPONDENT INFORMATION. List name and address of person filling out this form. Give telephone number and extension where person can be reached. Record the date this form was completed or updated. This information will not be published.

   Last Robinson First Jeffrey MI S.

   Address 778 Atlantic Drive

   City Atlanta State Georgia Zip 30332-0100

   Phone (404) 894-2834 Date 2-4-93

DOE F 1332.16 (10-84)
(Formerly RA-427)

OMB Approval
No. 1910-1400

U. S. DEPARTMENT OF ENERGY

UNIVERSITY CONTRACTOR, GRANTEE, AND COOPERATIVE AGREEMENT RECOMMENDATIONS FOR ANNOUNCEMENT AND DISTRIBUTION OF DOCUMENTS

See Instructions on Reverse Side

1. DOE Report No. 10	3. Title High Temperature Electrochemical Separation of H_2S from Coal Gasification Process Streams
2. DOE Contract No. DE-FG22-91PC91288	

4. Type of Document ("x" one)
- ☐ a. Scientific and technical report
- ☐ b. Conference paper:
  - Title of conference _____
  - Date of conference _____
  - Exact location of conference _____
  - Sponsoring organization _____
- ☒ c. Other (Specify) Notice of Energy RD&D Project

5. Recommended Announcement and Distribution ("x" one)
- ☒ a. Unrestricted unlimited distribution.
- ☐ b. Make available only within DOE and to DOE contractors and other U. S. Government agencies and their contractors.
- ☐ c. Other (Specify) _____

6. Reason for Recommended Restrictions

7. Patent and Copyright Information:
Does this information product disclose any new equipment, process, or material? ☐ No ☐ Yes If so, identify page nos. _____
Has an invention disclosure been submitted to DOE covering any aspect of this information product? ☐ No ☐ Yes
If so, identify the DOE (or other) disclosure number and to whom the disclosure was submitted.
Are there any patent-related objections to the release of this information product? ☐ No ☐ Yes If so, state these objections.
Does this information product contain copyrighted material? ☐ No ☐ Yes
If so, identify the page numbers _____ and attach the license or other authority for the government to reproduce.

8. Submitted by Name and Position (Please print or type) Jack Winnick, Professor		
Organization Georgia Tech Research Corporation		
Signature J.S.R.	Phone (404) 894-2839	Date 10-4-93

FOR DOE OR OTHER AUTHORIZED USE ONLY

9. Patent Clearance ("x" one)
- ☐ a. DOE patent clearance has been granted by responsible DOE patent group.
- ☐ b. Report has been sent to responsible DOE patent group for clearance.

DOE F 1430.22
(04-91)
All other editions
are obsolete
(Replaces DOE F 538)

OMB Control No.
1910-1400
Burden Disclosure
Statement on Back

U.S. DEPARTMENT OF ENERGY
NOTICE OF ENERGY RD&D PROJECT

1. DOE CONTRACT OR GRANT NUMBER DE-FG22-91PC91288

   ☐ New contract ☒ Continuation/Revision

2. A. NAME OF PERFORMING ORGANIZATION Georgia Tech Research Corporation

   B. Department or Division School of Chemical Engineering

   C. Street Address Bunger-Henry Building

   City Atlanta State Georgia Zip 30332-0100

   D. Type of Performing Organization (circle only one two-letter code)

   CU–College, university, or trade school
   EG–Electric or gas utility
   FF–Federally funded RD&D centers or laboratory operated for agency of US government
   IN–Private industry
   NP–Foundation or laboratory not operated for profit
   ST–Regional, state, or local government facility
   TA–Trade or professional organization
   US–Federal Agency
   XX–Other

3. PRINCIPAL OR SENIOR INVESTIGATOR

   A. Last Winnick First Jack MI S.

   B. Phone: Commercial (404) 894-2839 FTS

4. DOE SPONSORING OFFICE OR DIVISION Pittsburgh Energy & Technology Center

5. TITLE OF PROJECT High Temperature Electrochemical Separation of H_2S from Coal Gasification Process Streams.

6. DESCRIPTIVE SUMMARY (limit to 200 words)

Selective removal of H_2S from coal gas streams by a high temperature (650 °C) electrochemical operation is being perfected. The operation, which takes advantage of an electrochemical potential gradient rather than conventional techniques, removes H_2S from the coal gas stream, leaving H_2 to enrich the exiting gases. Sulfur is the by-product which is swept away by an inert sweep gas and condensed downstream.

Success in polishing the gasification stream (removing H_2S below 1ppm) leads future experimentation to material issues. Membrane/electrode stability & selectivity along with cell housing longevity using stainless steel characterize present studies.

7. RESPONDENT INFORMATION. List name and address of person filling out this form. Give telephone number and extension where person can be reached. Record the date this form was completed or updated. This information will not be published.

   Last Robinson First Jeffrey MI S.

   Address 778 Atlantic Drive

   City Atlanta State Georgia Zip 30332-0100

   Phone (404) 894-2834 Date 10-4-93

Georgia Tech

Office of Grants and Contracts Accounting

Georgia Institute of Technology
190 Bobby Dodd Way
Atlanta, Georgia 30332-0259
USA
404•894•4624; 2629
Fax: 404•894•5519

January 25, 1995

Ms. JoAnn C. Zysk, Contract Administrator
U. S. Department of Energy
Document Control Center
P. O. Box 10940, MS 921-118
Pittsburgh, PA 15236-0940

REFERENCE: Grant No. DE-FG22-91PC91288

Dear Ms. Zysk,

Enclosed are the original plus two (2) copies of the Federal Cash Transactions Report (SF-272) for Grant No. DE-FG22-91PC91288 covering the period October 01, 1994 through December 31, 1994.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch
Director

DVW/GMR/djt

Enclosures

c: Dr. Jack Winnick, Chemical Eng - 0100 (w/copy SF-269A)
Ms. Wanda Simon, OCA/CSD - 0420 (w/copy SF-269A)
File: E-19-683/R7311-0A0

FEDERAL CASH TRANSACTIONS REPORT

(See instructions on the back. If report is for more than one grant or assistance agreement, attach completed Standard Form 272-A.)

Approved by Office of Management and Budget, No. 80-R0182

1. Federal sponsoring agency and organizational element to which this report is submitted: U. S. DEPARTMENT OF ENERGY

2. RECIPIENT ORGANIZATION

Name : GEORGIA TECH RESEARCH CORPORATION

Number and Street : 400 10TH STREET, N.W. - ROOM 270

City, State and ZIP Code: ATLANTA, GA 30332-0415

3. FEDERAL EMPLOYER IDENTIFICATION NO. ▶ 58-0603146

4. Federal grant or other identification number: DE-FG22-91PC91288

5. Recipient's account number or identifying number: E-19-683/R7311-0A0

6. Letter of credit number:

7. Last payment voucher number:

Give total number for this period

8. Payment Vouchers credited to your account:

9. Treasury checks received (whether or not deposited): /

10. PERIOD COVERED BY THIS REPORT

FROM (month, day, year): October 01, 1994

TO (month, day, year): December 31, 1994

11. STATUS OF FEDERAL CASH (*See specific instructions on the back*)	
a. Cash on hand beginning of reporting period	$ (34,423.83)
b. Letter of credit withdrawals	-0-
c. Treasury check payments	29,551.25
d. Total receipts (*Sum of lines b and c*)	29,551.25
e. Total cash available (*Sum of lines a and d*)	4,872.58
f. Gross disbursements	11,868.75
g. Federal share of program income	-0-
h. Net disbursements (*Line f minus line g*)	11,868.75
i. Adjustments of prior periods	-0-
j. Cash on hand end of period	$ (16,741.33)

12. THE AMOUNT SHOWN ON LINE 11j, ABOVE, REPRESENTS CASH REQUIREMENTS FOR THE ENSUING *Days*	13. OTHER INFORMATION	
	a. Interest income	$
	b. Advances to subgrantees or subcontractors	$

14. REMARKS (*Attach additional sheets of plain paper, if more space is required*)

Questions concerning this report should be directed to:
Geraldine Reese (404) 894-2629

15. CERTIFICATION

I certify to the best of my knowledge and belief that this report is true in all respects and that all disbursements have been made for the purpose and conditions of the grant or agreement	AUTHORIZED CERTIFYING OFFICIAL	SIGNATURE	DATE REPORT SUBMITTED
		[signature]	January 25, 1995
		TYPED OR PRINTED NAME AND TITLE: David V. Welch, Director Grants and Contracts Accounting	TELEPHONE (*Area Code, Number, Extension*): (404) 894-2629

THIS SPACE FOR AGENCY USE

Georgia Tech

Office of Grants and Contracts Accounting

Georgia Institute of Technology
190 Bobby Dodd Way
Atlanta, Georgia 30332-0259
USA
404•894•4624; 2629
Fax: 404•894•5519

October 26, 1994

Ms. JoAnn C. Zysk, Contract Administrator
U. S. Department of Energy
Document Control Center
P. O. Box 10940, MS 921-118
Pittsburgh, PA 15236-0940

REFERENCE: Grant No. DE-FG22-91PC91287

Dear Ms. Zysk,

Enclosed are the original plus two (2) copies of the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) for Grant No. DE-FG22-91PC91288 covering the period July 01, 1994 through September 30, 1994.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch
Director

DVW/GMR/djt

Enclosures

c: Dr. Jack Winnick, Chemical Eng - 0100 (w/copy SF-269A)
Ms. Wanda Simon, OCA/CSD - 0420 (w/copy SF-269A)
File: E-19-683/R7311-0A0

FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

Federal Agency and Organizational Element to Which Report is Submitted	2. Federal Grant or Other Identifying Number Assigned By Federal Agency	OMB Approval No.	Page	of
U. S. DEPARTMENT OF ENERGY	DE-FG22-91PC91288	0348-0039	1	2 pages

Recipient Organization (Name and complete address, including ZIP code)

GEORGIA TECH RESEARCH CORPORATION
400 10TH STREET, N.W., RM 270
ATLANTA, GA 30332-0415

Employer Identification Number	5. Recipient Account Number or Identifying Number	6. Final Report	7. Basis
58-0603146	E-19-683/R7311-0A0	☐ Yes ☒ No	☒ Cash ☐ Accrual

Funding/Grant Period (See Instructions) From: (Month, Day, Year)	To: (Month, Day, Year)	9. Period Covered by this Report From: (Month, Day, Year)	To: (Month, Day, Year)
September 01, 1991	December 31, 1994	July 01, 1994	September 30, 1994

Transactions:	I Previously Reported	II This Period	III Cumulative
a. Total outlays	117,390.26	43,842.63	161,232.89
b. Recipient share of outlays	-0-	-0-	-0-
c. Federal share of outlays	117,390.26	43,842.63	161,232.89
d. Total unliquidated obligations			11,173.69
e. Recipient share of unliquidated obligations			-0-
f. Federal share of unliquidated obligations			11,173.69
g. Total Federal share *(Sum of lines c and f)*			172,406.58
h. Total Federal funds authorized for this funding period			199,977.00
i. Unobligated balance of Federal funds *(Line h minus line g)*			27,570.42

Indirect Expense	a. Type of Rate *(Place "X" in appropriate box)* ☐ Provisional ☐ Predetermined ☐ Final ☐ Fixed			
	b. Rate	c. Base	d. Total Amount	e. Federal Share
	SEE ATTACHED	MTDC	12,496.95	12,496.95

Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.

Questions concerning this report should be directed to: Geraldine Reese (404) 894-2629

GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30

Certification: **I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.**

Typed or Printed Name and Title	Telephone (Area code, number and extension)
David V. Welch, Director, Grants and Contracts Accounting	(404) 894-2629
Signature of Authorized Certifying Official	Date Report Submitted
	October 26, 1994

Attachment

Financial Status Report (10/26/94)
U. S. Department of Energy
Grant No. DE-FG22-91PC91288 (E-19-683/R7311-0A0)
Period Covering: 07/01/94 - 09/30/94

	Direct Costs	Indirect Costs	Equipment
FY92 @ 61.5% Fixed	$29,146.09	$ 5,635.96	$19,981.92
FY93 @ 55.2% Provisional	30,904.44	17,059.25	
FY94 @ 37.0% Provisional	25,287.97	9,356.55	
FY95 @ 40.0% Provisional	31,345.68	12,496.95 (1)	

REPORT PERIOD

	Direct Costs	Indirect Costs
07/01/94 - 09/30/94	$31,345.68	$12,496.95 (1)

(1) Includes an adjustment of $41.32 for FY94

Georgia Tech

Office of Grants and Contracts Accounting

Georgia Institute of Technology
190 Bobby Dodd Way
Atlanta, Georgia 30332-0259
USA
404•894•4624; 2629
Fax: 404•894•5519

August 5, 1994

Ms. JoAnn C. Zysk, Contract Administrator
U. S. Department of Energy
Document Control Center
P. O. Box 10940, MS 921-118
Pittsburgh, PA 15236-0940

REFERENCE: Grant No. DE-FG22-91PC91287

Dear Ms. Zysk,

Enclosed are the original plus two (2) copies of the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) for Grant No. DE-FG22-91PC91288 covering the period April 01, 1994 through June 30, 1994.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch
Director

DVW/GMR/djt

Enclosures

c: Dr. Jack Winnick, Chemical Eng - 0100 (w/copy SF-269A)
Ms. Wanda Simon, OCA/CSD - 0420 (w/copy SF-269A)
File: E-19-683/R7311-0A0

FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

1. Federal Agency and Organizational Element to Which Report is Submitted	2. Federal Grant or Other Identifying Number Assigned By Federal Agency	OMB Approval No.	Page	of
U. S. DEPARTMENT OF ENERGY	DE-FG22-91PC91288	0348-0039	1	2 pages

3. Recipient Organization (Name and complete address, including ZIP code)

GEORGIA TECH RESEARCH CORPORATION
P. O. BOX 100117
ATLANTA, GA 30384

4. Employer Identification Number	5. Recipient Account Number or Identifying Number	6. Final Report	7. Basis
58-0603146	E-19-683/R7311-0A0	☐ Yes ☒ No	☒ Cash ☐ Accrual

8. Funding/Grant Period (See Instructions) From: (Month, Day, Year)	To: (Month, Day, Year)	9. Period Covered by this Report From: (Month, Day, Year)	To: (Month, Day, Year)
September 01, 1991	December 31, 1994	April 01, 1994	June 30, 1994

10. Transactions:	I Previously Reported	II This Period	III Cumulative
a. Total outlays	102,969.69	14,420.57	117,390.26
b. Recipient share of outlays	-0-	-0-	-0-
c. Federal share of outlays	102,969.69	14,420.57	117,390.26
d. Total unliquidated obligations			971.54
e. Recipient share of unliquidated obligations			-0-
f. Federal share of unliquidated obligations			971.54
g. Total Federal share *(Sum of lines c and f)*			118,361.80
h. Total Federal funds authorized for this funding period			199,977.00
i. Unobligated balance of Federal funds *(Line h minus line g)*			81,615.20

11. Indirect Expense	a. Type of Rate *(Place "X" in appropriate box)* ☒ Provisional ☒ Predetermined ☐ Final ☐ Fixed			
	b. Rate	c. Base	d. Total Amount	e. Federal Share
	SEE ATTACHED	MTDC	3,894.61	3,894.61

12. *Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.*

Questions concerning this report should be directed to:
Geraldine Reese (404) 894-2629

GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30

13. Certification: **I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.**

Typed or Printed Name and Title	Telephone (Area code, number and extension)
David V. Welch, Director, Grants and Contracts Accounting	(404) 894-2629
Signature of Authorized Certifying Official	**Date Report Submitted**
	August 5, 1994

Attachment

Financial Status Report (08/05/94)
U. S. Department of Energy
Grant No. DE-FG22-91PC91288 (E-19-683/R7311-0A0)
Period Covering: 04/01/94 - 06/30/94

	Direct Costs	Indirect Costs	Equipment
FY92 @ 61.5% Fixed	$29,146.09	$ 5,635.96	$19,981.92
FY93 @ 55.2% Provisional	30,904.44	17,059.25	
FY94 @ 37.0% Provisional	25,287.97	9,356.55	

REPORT PERIOD

	Direct Costs	Indirect Costs
04/01/94 - 06/30/94	$10,525.96	$ 3,894.61

Georgia Tech

E-19-683
N/a
Office of Grants and Contracts Accounting

Georgia Institute of Technology
190 Bobby Dodd Way
Atlanta, Georgia 30332-0259
USA
404•894•4624; 2629
Fax: 404•894•5519

January 19, 1994

Ms. JoAnn C. Zysk, Contract Administrator
U. S. Department of Energy
Document Control Center
P. O. Box 10940, MS 921-118
Pittsburgh, PA 15236-0940

REFERENCE: Grant No. DE-FG22-91PC91288

Enclosed are the original plus two (2) copies of the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) for Grant Number DE-FG22-91PC91288 covering the period October 01, 1993 through December 31, 1993.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch
Director

DVW/GMR/djt

Enclosures

c: Dr. Jack Winnick, Chemical Eng - 0100 (w/copy SF-269A)
Ms. Wanda Simon, OCA/CSD - 0420 (w/copy SF-269A)
File: E-19-683/R7311-0A0

FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

1. Federal Agency and Organizational Element to Which Report is Submitted	2. Federal Grant or Other Identifying Number Assigned By Federal Agency	OMB Approval No.	Page	of
U. S. DEPARTMENT OF ENERGY	DE-FG22-91PC91288	0348-0039	1	2 pages

3. Recipient Organization (Name and complete address, including ZIP code)

GEORGIA TECH RESEARCH CORPORATION
P. O. BOX 100117
ATLANTA, GA 30384

4. Employer Identification Number	5. Recipient Account Number or Identifying Number	6. Final Report	7. Basis
58-0603146	E-19-683/R7311-0A0	☐ Yes ☒ No	☒ Cash ☐ Accrual

8. Funding/Grant Period (See Instructions) From: (Month, Day, Year)	To: (Month, Day, Year)	9. Period Covered by this Report From: (Month, Day, Year)	To: (Month, Day, Year)
September 01, 1991	August 31, 1994	October 01, 1993	December 31, 1993

10. Transactions:	I Previously Reported	II This Period	III Cumulative
a. Total outlays	90,321.50	6,646.50	96,968.00
b. Recipient share of outlays	-0-	-0-	-0-
c. Federal share of outlays	90,321.50	6,646.50	96,968.00
d. Total unliquidated obligations			525.47
e. Recipient share of unliquidated obligations			-0-
f. Federal share of unliquidated obligations			525.47
g. Total Federal share *(Sum of lines c and f)*			97,493.47
h. Total Federal funds authorized for this funding period			199,977.00
i. Unobligated balance of Federal funds *(Line h minus line g)*			102,483.53

11. Indirect Expense	a. Type of Rate *(Place "X" in appropriate box)* ☒ Provisional ☐ Predetermined ☐ Final ☐ Fixed			
	b. Rate	c. Base	d. Total Amount	e. Federal Share
	SEE ATTACHED	MTDC	1,795.04	1,795.04

12. *Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.*

Questions pertaining to this report should be directed to: Geraldine Reese (404) 894-2629

GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30

13. Certification: **I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.**

Typed or Printed Name and Title	Telephone (Area code, number and extension)
David V. Welch, Director, Grants and Contracts Accounting	(404) 894-2629
Signature of Authorized Certifying Official	**Date Report Submitted**
	January 19, 1994

Attachment

Financial Status Report (01/19/94)
U. S. Department of Energy
Grant No. DE-FG22-91PC91288 (E-19-683/R7311-0A0)
Period Covering: 10/01/93 - 12/31/93

	Direct Costs	Indirect Costs	Equipment
FY92 @ 61.5% Fixed	29,146.09	5,635.96	19,981.92
FY93 @ 55.2% Provisional	30,904.44	17,059.25	
FY94 @ 37.0% Provisional	10,381.21	3,841.05	

REPORT PERIOD

	Direct Costs	Indirect Costs
10/01/93 - 12/31/93	4,851.46	1,795.04

FEDERAL CASH TRANSACTIONS REPORT

(See instructions on the back. If report is for more than one grant or assistance agreement, attach completed Standard Form 272-A.)

Approved by Office of Management and Budget, No. 80-R0182

1. Federal sponsoring agency and organizational element to which this report is submitted: U. S. DEPARTMENT OF ENERGY

2. RECIPIENT ORGANIZATION

Name: GEORGIA TECH RESEARCH CORPORATION

Number and Street: P. O. BOX 100117

City, State and ZIP Code: ATLANTA, GA 30384

3. FEDERAL EMPLOYER IDENTIFICATION NO. ▶ 58-0603146

4. Federal grant or other identification number: DE-FG22-91PC91288

5. Recipient's account number or identifying number: E-19-683/R7311-0A0

6. Letter of credit number

7. Last payment voucher number

Give total number for this period

8. Payment Vouchers credited to your account

9. Treasury checks received (whether or not deposited)

10. PERIOD COVERED BY THIS REPORT

FROM (month, day, year): October 01, 1993

TO (month, day, year): December 31, 1993

11. STATUS OF FEDERAL CASH (See specific instructions on the back)	
a. Cash on hand beginning of reporting period	$ (15,991.40)
b. Letter of credit withdrawals	-0-
c. Treasury check payments	15,088.27
d. Total receipts (*Sum of lines b and c*)	15,088.27
e. Total cash available (*Sum of lines a and d*)	(903.13)
f. Gross disbursements	6,646.50
g. Federal share of program income	-0-
h. Net disbursements (*Line f minus line g*)	6,646.50
i. Adjustments of prior periods	-0-
j. Cash on hand end of period	$ (7,549.63)

12. THE AMOUNT SHOWN ON LINE 11J, ABOVE, REPRESENTS CASH REQUIREMENTS FOR THE ENSUING *Days*	13. OTHER INFORMATION	
	a. Interest income	$
	b. Advances to subgrantees or subcontractors	$

14. REMARKS (*Attach additional sheets of plain paper, if more space is required*)

Questions pertaining to this report should be directed to:
Geraldine Reese (404) 894-2629

15. CERTIFICATION

I certify to the best of my knowledge and belief that this report is true in all respects and that all disbursements have been made for the purpose and conditions of the grant or agreement

AUTHORIZED CERTIFYING OFFICIAL

SIGNATURE

DATE REPORT SUBMITTED: January 19, 1994

TYPED OR PRINTED NAME AND TITLE: David V. Welch, Director
Grants and Contracts Accounting

TELEPHONE (*Area Code, Number, Extension*): (404) 894-2629

THIS SPACE FOR AGENCY USE

Georgia Tech

Office of Grants and Contracts Accounting

Georgia Institute of Technology
Hinman Building
Atlanta, Georgia 30332-0259
USA
404•894•4624; 2629
Fax: 404•894•5519

E-19-683 N/A

October 20, 1993

Ms. JoAnn C. Zysk, Contract Administrator
U. S. Department of Energy
Document Control Center
P. O. Box 10940, MS 921-118
Pittsburgh, PA 15236-0940

REFERENCE: DE-FG22-91PC91288

Dear Ms. Zysk,

Enclosed are the original plus two (2) copies of the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) for Grant No. DE-FG22-91PC91288 covering the period July 01, 1993 through September 30, 1993.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch
Director

DVW/GMR/djt

Enclosures

c: Dr. Jack Winnick, Chemical Eng - 0100 (w/copy SF-269A)
Ms. Wanda Simon, OCA/CSD - 0420 (w/copy SF-269A)
File: E-19-683/R7311-0A0

RECEIVED
OCT 27 1993
OFFICE OF CONTRACT ADMINISTRATION

FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

1. Federal Agency and Organizational Element to Which Report is Submitted	2. Federal Grant or Other Identifying Number Assigned By Federal Agency	OMB Approval No.	Page	of
U. S. DEPARTMNET OF ENERGY	DE-FG22-91PC91288	0348-0039	1	2 pages

3. Recipient Organization (Name and complete address, including ZIP code)
GEORGIA TECH RESEARCH CORPORATION
P. O. BOX 100117
ATLANTA, GA 30384

4. Employer Identification Number	5. Recipient Account Number or Identifying Number	6. Final Report	7. Basis
58-0603146	E-19-683/R7311-0A0	☐ Yes ☒ No	☒ Cash ☐ Accrual

8. Funding/Grant Period (See Instructions) From: (Month, Day, Year)	To: (Month, Day, Year)	9. Period Covered by this Report From: (Month, Day, Year)	To: (Month, Day, Year)
September 01, 1991	August 31, 1994	July 01, 1993	September 30, 1993

10. Transactions:	I Previously Reported	II This Period	III Cumulative
a. Total outlays	82,745.74	7,575.76	90,321.50
b. Recipient share of outlays	-0-	-0-	-0-
c. Federal share of outlays	82,745.74	7,575.76	90,321.50
d. Total unliquidated obligations			15,827.78
e. Recipient share of unliquidated obligations			-0-
f. Federal share of unliquidated obligations			15,827.78
g. Total Federal share *(Sum of lines c and f)*			106,149.28
h. Total Federal funds authorized for this funding period			199,977.00
i. Unobligated balance of Federal funds *(Line h minus line g)*			93,827.72

11. Indirect Expense	a. Type of Rate *(Place "X" in appropriate box)* ☒ Provisional ☐ Predetermined ☐ Final ☐ Fixed			
	b. Rate	c. Base	d. Total Amount	e. Federal Share
	SEE ATTACHED	MTDC	2,046.01	2,046.01

12. *Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.*

Questions pertaining to this report should be directed to: Geraldine Reese (404) 894-2629

GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30

13. Certification: **I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.**

Typed or Printed Name and Title	Telephone (Area code, number and extension)
David V. Welch, Director, Grants and Contracts Accounting	(404) 894-2629
Signature of Authorized Certifying Official	**Date Report Submitted**
	October 20, 1993

Attachment

Financial Status Report (10/20/93)
U. S. Department of Energy
Grant No. DE-FG22-91PC91288 (E-19-683/R7311-0A0)
Period Covering: 07/01/93 - 09/30/93

	Direct Costs	Indirect Costs	Equipment
FY92 @ 61.5% Fixed	29,146.09	5,635.96	19,981.92
FY93 @ 55.2% Provisional	30,904.44	17,059.25	
FY94 @ 37.0% Provisional	5,529.75	2,046.01	

REPORT PERIOD

	Direct Costs	Indirect Costs
07/01/93 - 09/30/93	5,529.75	2,046.01

FEDERAL CASH TRANSACTIONS REPORT

(See instructions on the back. If report is for more than one grant or assistance agreement, attach completed Standard Form 272-A.)

Approved by Office of Management and Budget, No. 80-R0182

1. Federal sponsoring agency and organizational element to which this report is submitted: U. S. DEPARTMENT OF ENERGY

2. RECIPIENT ORGANIZATION

Name: GEORGIA TECH RESEARCH CORPORATION

Number and Street: P. O. BOX 100117

City, State and ZIP Code: ATLANTA, GA 30384

3. FEDERAL EMPLOYER IDENTIFICATION NO. ▶ 58-0603146

4. Federal grant or other identification number: DE-FG22-91PC91288

5. Recipient's account number or identifying number: E-19-683/R7311-0A0

6. Letter of credit number:

7. Last payment voucher number:

Give total number for this period

8. Payment Vouchers credited to your account:

9. Treasury checks received (whether or not deposited):

10. PERIOD COVERED BY THIS REPORT

FROM (month, day, year): July 01, 1993

TO (month, day year): September 30, 1993

11. STATUS OF FEDERAL CASH (See specific instructions on the back)	
a. Cash on hand beginning of reporting period	$(24,021.62)
b. Letter of credit withdrawals	-0-
c. Treasury check payments	15,605.98
d. Total receipts (*Sum of lines b and c*)	15,605.98
e. Total cash available (*Sum of lines a and d*)	(8,415.64)
f. Gross disbursements	7,575.76
g. Federal share of program income	-0-
h. Net disbursements (*Line f minus line g*)	7,575.76
i. Adjustments of prior periods	-0-
j. Cash on hand end of period	$(15,991.40)

12. THE AMOUNT SHOWN ON LINE 11j, ABOVE, REPRESENTS CASH REQUIREMENTS FOR THE ENSUING *Days*

13. OTHER INFORMATION	
a. Interest income	$
b. Advances to subgrantees or subcontractors	$

14. REMARKS (*Attach additional sheets of plain paper, if more space is required*)

Questions pertaining to this report should be directed to: Geraldine Reese (404) 894-2629

15. CERTIFICATION

I certify to the best of my knowledge and belief that this report is true in all respects and that all disbursements have been made for the purpose and conditions of the grant or agreement

AUTHORIZED CERTIFYING OFFICIAL

SIGNATURE

DATE REPORT SUBMITTED: October 20, 1993

TYPED OR PRINTED NAME AND TITLE: David V. Welch, Director
Grants and Contracts Accounting

TELEPHONE (*Area Code, Number, Extension*): (404) 894-2629

THIS SPACE FOR AGENCY USE

Georgia Tech

Office of Grants and Contracts Accounting

Georgia Institute of Technology
190 Bobby Dodd Way
Atlanta, Georgia 30332-0259
USA
404•894•4624; 2629
Fax: 404•894•5519

RECEIVED
AUG 12 1993
OFFICE OF CONTRACT ADMINISTRATION

August 6, 1993

Ms. JoAnn C. Zysk, Contract Administrator
U. S. Department of Energy
Document Control Center
P. O. Box 10940, MS 921-118
Pittsburgh, PA 15236-0940

REFERENCE: DE-FG22-91PC91288

Dear Ms. Zysk,

Enclosed are the original plus two (2) copies of the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) for Grant No. DE-FG22-91PC91288 covering the period April 01, 1993 through June 30, 1993.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch
Director

DVW/GMR/djt

Enclosures

c: Dr. Jack Winnick, Chemical Eng - 0100 (w/copy SF-269A)
Ms. Wanda Simon, OCA/CSD - 0420 (w/copy SF-269A)
File: E-19-683/R7311-0A0

FINANCIAL STATUS REPORT
(Short Form)
(Follow instructions on the back)

Federal Agency and Organizational Element to Which Report is Submitted	2. Federal Grant or Other Identifying Number Assigned By Federal Agency	OMB Approval No.	Page	of
. S. DEPARTMENT OF ENERGY	DE-FG22-91PC91288	0348-0039	1	2 pages

Recipient Organization (Name and complete address, including ZIP code)
GEORGIA TECH RESEARCH CORPORATION
P. O. BOX 100117
ATLANTA, GA 30384

Employer Identification Number	5. Recipient Account Number or Identifying Number	6. Final Report	7. Basis
58-0603146	E-19-683/R7311-0A0	☐ Yes ☒ No	☒ Cash ☐ Accrual

Funding/Grant Period (See instructions) From: (Month, Day, Year)	To: (Month, Day, Year)	9. Period Covered by this Report From: (Month, Day, Year)	To: (Month, Day, Year)
September 01, 1991	August 31, 1994	April 01, 1993	June 30, 1993

Transactions:	I Previously Reported	II This Period	III Cumulative
Total outlays	63,056.34	19,689.40	82,745.74
Recipient share of outlays	-0-	-0-	-0-
Federal share of outlays	63,056.34	19,689.40	82,745.74
Total unliquidated obligations			761.61
Recipient share of unliquidated obligations			-0-
Federal share of unliquidated obligations			761.61
Total Federal share (Sum of lines c and f)			83,507.35
Total Federal funds authorized for this funding period			119,977.00
Unobligated balance of Federal funds (Line h minus line g)			116,469.65

Indirect Expense	a. Type of Rate (Place "X" in appropriate box) ☒ Provisional ☐ Predetermined ☐ Final ☒ Fixed			
	b. Rate	c. Base	d. Total Amount	e. Federal Share
	SEE ATTACHED	MTDC	7,002.93	7,002.93

Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.

Questions pertaining to this report should be directed to: Geraldine Reese (404) 894-2629

EORGIA TECH'S FISCAL YEAR ENDS JUNE 30

Certification: I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.

Typed or Printed Name and Title	Telephone (Area code, number and extension)
vid V. Welch, Director, Grants and Contracts Accounting	(404) 894-2629
Signature of Authorized Certifying Official	Date Report Submitted
	August 6, 1993

ıancial Status Report (08/06/93)
. S. Department of Energy
Grant No. DE-FG22-91PC91288 (E19-683/R7311-0A0)
Period Covering: 04/01/93 - 06/30/93

FY92 @ 61.5% - Fixed
FY93 @ 55.2% - Provisional

	Direct Costs	Indirect Costs	Equipment
FY92	29,146.09	5,635.96	19,981.92
FY93	30,904.44	17,059.25	

REPORT PERIOD

	Direct Costs	Indirect Costs
04/01/93 - 06/30/93	12,686.47	7,002.93

Georgia Tech

Office of Grants and Contracts Accounting

Georgia Institute of Technology
Hinman Building
Atlanta, Georgia 30332-0259
404•894•4624; 2629
Fax: 404•894•5519

May 20, 1992

Ms. JoAnn C. Zysk, Contract Administrator
AD-22, MS 921-118
U. S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236-0940

REFERENCE: DE-FG22-91PC91288

Dear Ms. Zysk,

Enclosed are the original Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) for Grant No. DE-FG22-91PC91288 covering the period January 01, 1992 through March 31, 1992 with copies being distributed in accordance to the Federal Assistance Reporting Checklist.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch, Director

DVW/GMR/djt

Enclosures

c: Ms. Marilyn Keane (w/copy SF-269A)
PM-01-MS 922-206
U. S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

William Maro (w/copy SF-269A & SF-272)
Budget and Financial Management
AD-30, MS 921-232
U. S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

Dr. Jack Winnick, Chemical Eng. - 0100 (w/copy SF-269A)
Ms. Mary Wolfe, OCA/CSD - 0420 (w/copy SF-269A)
File: E-19-683/R7311-0A0

FINANCIAL STATUS REPORT
(Short Form)
(Follow instructions on the back)

Federal Agency and Organizational Element to Which Report is Submitted	2. Federal Grant or Other Identifying Number Assigned By Federal Agency	OMB Approval No.	Page	of
U. S. DEPARTMENT OF ENERGY	DE-FG22-91PC91288	0348-0039	1	1 pages

Recipient Organization (Name and complete address, including ZIP code)
GEORGIA TECH RESEARCH CORPORATION
P. O. BOX 100117
ATLANTA, GA 30384

Employer Identification Number	5. Recipient Account Number or Identifying Number	6. Final Report	7. Basis
58-0603146	E-19-683/R7311-0A0	☐ Yes ☒ No	☒ Cash ☐ Accrual

Funding/Grant Period (See Instructions) From: (Month, Day, Year)	To: (Month, Day, Year)	9. Period Covered by this Report From: (Month, Day, Year)	To: (Month, Day, Year)
September 01, 1991	August 31, 1994	January 01, 1992	March 31, 1992

10. Transactions:	I Previously Reported	II This Period	III Cumulative
a. Total outlays	3,206.36	9,283.63	12,489.99
b. Recipient share of outlays	-0-	-0-	-0-
c. Federal share of outlays	3,206.36	9,283.63	12,489.99
d. Total unliquidated obligations			23,733.29
e. Recipient share of unliquidated obligations			-0-
f. Federal share of unliquidated obligations			23,733.29
g. Total Federal share (*Sum of lines c and f*)			36,223.28
h. Total Federal funds authorized for this funding period			199,977.00
i. Unobligated balance of Federal funds (*Line h minus line g*)			163,753.72

11. Indirect Expense	a. Type of Rate (*Place "X" in appropriate box*) ☒ Provisional ☐ Predetermined ☐ Final ☐ Fixed			
	b. Rate	c. Base	d. Total Amount	e. Federal Share
	FY92 @ 61.5%	MTDC	3,966.49	3,966.49

12. *Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.*

Questions pertaining to this report should be directed to: Geraldine Reese (404) 894-2629

GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30.

13. Certification: **I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.**

Typed or Printed Name and Title	Telephone (Area code, number and extension)
David V. Welch, Director, Grants and Contracts Accounting	(404) 894-2629
Signature of Authorized Certifying Official	**Date Report Submitted**
	May 20, 1992

SN 7540-01-218-4387	Direct Costs	Indirect Costs
09/01/91-12/31/91	1,985.36	1,221.00
01/01/92-03/31/92	6,538.14	2,745.49

Standard Form 269A (REV 4-88)
Prescribed by OMB Circulars A-102 and A-110

E19-683

DOE F 1332.16 (10-84)
(Formerly RA-427)

OMB Approval
No. 1910-1400

U. S. DEPARTMENT OF ENERGY

UNIVERSITY CONTRACTOR, GRANTEE, AND COOPERATIVE AGREEMENT RECOMMENDATIONS FOR ANNOUNCEMENT AND DISTRIBUTION OF DOCUMENTS

See Instructions on Reverse Side

1. DOE Report No. 2

2. DOE Contract No. DE-AS22-91PC91282

3. Title High Temperature Electrochemical Separation of H_2S from Coal Gasification

4. Type of Document ("x" one)
   - ☒ a. Scientific and technical report
   - ☐ b. Conference paper:
     - Title of conference _____
     - Date of conference _____
     - Exact location of conference _____
     - Sponsoring organization _____
   - ☐ c. Other (Specify) _____

5. Recommended Announcement and Distribution ("x" one)
   - ☒ a. Unrestricted unlimited distribution.
   - ☐ b. Make available only within DOE and to DOE contractors and other U. S. Government agencies and their contractors.
   - ☐ c. Other (Specify) _____

6. Reason for Recommended Restrictions

7. Patent and Copyright Information:
   Does this information product disclose any new equipment, process, or material? ☐ No ☐ Yes If so, identify page nos. _____
   Has an invention disclosure been submitted to DOE covering any aspect of this information product? ☐ No ☐ Yes
   If so, identify the DOE (or other) disclosure number and to whom the disclosure was submitted.
   Are there any patent-related objections to the release of this information product? ☐ No ☐ Yes If so, state these objections.
   Does this information product contain copyrighted material? ☐ No ☐ Yes
   If so, identify the page numbers _____ and attach the license or other authority for the government to reproduce.

8. Submitted by — Name and Position (Please print or type)
   Jack Winnick, Professor

   Organization
   Georgia Tech Research Corp.

   Signature / / / /

   Phone (404) 894-2834

   Date 2/10/92

FOR DOE OR OTHER AUTHORIZED USE ONLY

9. Patent Clearance ("x" one)
   - ☐ a. DOE patent clearance has been granted by responsible DOE patent group.
   - ☐ b. Report has been sent to responsible DOE patent group for clearance.

Quarterly Progress Report:

High Temperature Electrochemical Separation Of H_2S from Coal Gasification Process Streams

Grant DE-PS22-91PC91282

October 1, 1991 - December 31, 1991

by

Professor Jack Winnick

Georgia Institute of Technology

School of Chemical Engineering

Atlanta, Georgia 30332-0100

Purpose and Goals of Research

An advanced process for the separation of hydrogen sulfide from coal gasification product streams through an electrochemical membrane is being developed using the funds from this grant. H_2S is removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. The process allows removal of H_2S without cooling the gas stream and with negligible pressure loss through the separator. The process is economically attractive by the lack of adsorbents and the lack of a Claus process for sulfur recovery.

Research conducted during the present quarter is here highlighted, with an emphasis on progress towards the goal of an economically viable H_2S removal technology for use in coal gasification facilities providing polished fuel for co-generation coal fired electrical power facilities and Molten Carbonate Fuel Cell electrical power facilities.

Introduction

The process under development is presented schematically in Figure 1. The process gas, cleaned of particulates, is passed by the cathode. Here, the most easily reduced species will be electronated; under these conditions, it is H_2S:

$$H_2S + 2\,e^- \rightarrow S^{2-} + H_2 \tag{1}$$

The sulfide ions are maintained, with alkali-metal cations, as a fused electrolyte in a ceramic membrane. The sulfide is transported across to the anode, where it is oxidized to elemental sulfur. An inert gas such as N_2 is used at the anode to carry away the vaporous sulfur, S_2, to be condensed for recovery downstream.

$$S^{2-} \rightarrow \frac{1}{2}S_2 + 2\,e^- \tag{2}$$

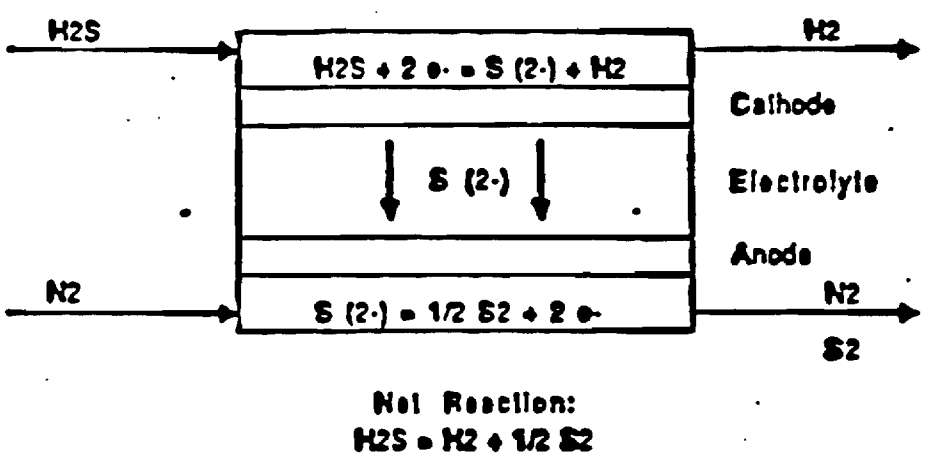

Figure 1.
Schematic of H_2S Removal Cell.

Feasibility Calculations

The following is a comparison of electrochemical cell stack sizes of an Electrochemical Membrane Separator (EMS) with a Molten Carbonate Fuel Cell (MCFC). The facilities each process 10MM SCFD of coal synthesis gas with the following composition presented in Table 1.

Table 1.
Coal Synthesis Gas Composition

CH_4:	0.3 vol%
H_2:	29.8 vol%
CO:	41.0 vol%
CO_2:	10.2 vol%
H_2S:	100 ppmv
COS:	in equilibrium
N_2:	0.7 vol%
H_2O:	17.1 vol%

The gases are supplied to the EMS and the MCFC facilities at 650°C and 1 atm. In order to be an economically viable process, the EMS must be substantially smaller in size than the MCFC and consume only a fraction of the produced power.

EMS Calculations

The calculations for the EMS are based on a volumetric flow rate of 10MM SCFD or 3.3×10^6 cm^3/sec. This flow is equally divided into each cell in the EMS stack and then sub-divided into parallel gas flow channels above the cathode with dimensions of 0.3 cm by 0.3 cm. With this, the equivalent channel diameter is calculated by equation (3).

$$D_{eq} = 4*r_H = 4*[\frac{cross\ sectional\ area}{wetted\ perimeter}] = 0.3\ cm \tag{3}$$

Initially, laminar flow is assumed in each channel. Thus, from Incropera and DeWitt[1],

$$N_{Sh} = k_m*\frac{D_{eq}}{D_{AB}} = 2.98 \tag{4}$$

From Reid, Prausnitz, and Poling[2]:

$$D_{AB} = [\frac{0.0018583*T^{3/2}}{P*\sigma^2_{AB}*\Omega_{D,AB}}]*[\frac{1}{M_A} + \frac{1}{M_B}]^{1/2} \tag{5}$$

with A = CO and B = H_2S. If P = 1 atm, T = 923 K, σ_{AB} = 3.657, $\Omega_{D,AB}$ = 0.82, M_A = 28, and M_B = 34 then D_{AB} = 1.2 cm^2/sec. Thus, by applying equation (4), the mass transfer coefficient for the gas phase diffusion can be found to be k_m = 12.0 cm/sec.

The gas-phase limiting current density is the maximum current density which the cell can support as dictated by the maximum rate of diffusion of reagent to the sites of the electrochemical reaction. In this case, this reagent is H_2S by the reaction:

$$H_2S + 2\ e^- \rightarrow S^{2-} + H_2 \tag{1}$$

The flux of material to the electrode/electrolyte interface (neglecting pore diffusion, which has been shown to be negligible) is defined as:

$$N_{H_2S} = k_m \rho \frac{(y_{feed} - y_{out})}{\ln(\frac{y_{feed}}{y_{out}})} \tag{7}$$

where ρ is the molar density of the gas phase (at 650°C and 1 atm this is 1.32 x 10^{-5} gmole/cm^3). The current density supported by this diffusion is thus,

$$i_{d,H_2S} = nFN_{H_2S} \tag{7}$$

By combining equations (6) and (7), the current density can be calculated as follows:

$$i_{d,H_2S} = nFk_m \rho (\frac{y_{feed} - y_{out}}{\ln \frac{y_{feed}}{y_{out}}}) \tag{8}$$

With n = 2 faradays/equivalent and F = 96500 coulombs/equivalent, the limiting current density for the 1st stack which removes H_2S from 100 ppmv to 10 ppmv is 1.2 mA/cm^2.

There is a direct relationship between the amount of H_2S removed and the total current applied to the cell. This is defined by equation (9):

$$I = nFm(y_{feed} - y_{out}) \tag{9}$$

where m is the total molar flowrate of the gas to the removal cell. At 10MM SCFD, m = 134 gmole/sec. Thus, for the 1st stack of removal cells (100ppmv to 10 ppmv), the total current required is 2.33×10^3 Amps. If the driving potential to maintain this current is around 1 volt, this translates to 2.33 kWatts.

The active membrane surface area can be found by dividing the total required current by the maximum gas phase limiting current density:

$$A = \frac{I}{i_{d,H_2S}} \tag{10}$$

With $I = 2.33 \times 10^3$ Amps and $i_{d,H2S} = 1.2 \times 10^{-3}$ Amps/cm^2, the total stack surface area is 1.96×10^6 cm^2 (or 2099 ft^2). MCFC membranes are commonly available as 4 ft by 4 ft squares. If the same technology for the manufacture of these membranes is applied to the EMS membranes, then the total number of 4 ft by 4 ft electrochemical cells in the first stack is 131.

Since there are 131 individual cells in the first stack, the total molar flowrate is divided evenly into each cell in the stack. Therefore, the molar flowrate to each individual cell is 1.02 gmole/sec. Since the cell is 4 ft wide, there will be 406 individual parallel flow channels above the surface of each cathode and anode. The molar flowrate in each channel is thus 2.5×10^{-3} gmole/sec. This corresponds to a volumetric flowrate of 1.89×10^2 cm^3/sec through each channel. The gas velocity is

found by dividing the volumetric flow through the channel by the channel cross sectional area. For a 0.3 cm by 0.3 cm square channel, this corresponds to a velocity of 21 meters/sec. The Reynolds Number for this flow is found to be 573, which verifies the original assumption of laminar flow. The cell residence time is thus found to be 0.058 seconds.

The calculations for the second EMS stack (10 ppmv to 1 ppmv) are identical to the calculations for the first. The results of this analysis show the limiting current density to be 0.12 mA/cm^2. The total applied current is 2.33×10^2 Amps (0.23 kWatts) and the required surface area is identical to the first stack, 2099 ft (131 individual membranes).

As a check of the mass transfer and cell residence time calculations, total molar transport through the membrane over the period of the cell residence time was calculated based on the mass flux estimation of current density and compared to a material balance around the cathode side of the cell. Multiplying the mass flux through the membrane by the membrane area and the cell residence time gives 6.97×10^{-4} gmoles of material transported (100 ppmv to 10 ppmv cell). Multiplying the molar flowrate by cell residence time and concentration change gives 6.94×10^{-4} gmoles of material transported. This confirms the residence time estimation to within 0.3%.

A summary of the EMS design calculations follows in Table 2.

Table 2.
Summary of EMS Design Calculations.

Gas Phase Mass Transfer Coefficient, k_m:	12.0 cm/sec
Current Density in 1st Stack:	1.2 mA/cm^2
Total Current to 1st Stack:	2330 Amps
Area of 1st Stack:	2099 ft^2
Individual 4 ft x 4 ft Cells in 1st Stack:	131
Current Density in 2nd Stack:	0.120 mA/cm^2
Total Current to 2nd Stack:	233.0 Amps
Area of 2nd Stack:	2099 ft^2
Individual 4 ft x 4 ft Cells in 2nd Stack:	131
Total EMS Area:	4198 ft^2
Gas Velocity in Each Channel:	21 m/sec
Total Cell Residence Time:	0.116 sec*
Reynold's Number:	574
Total EMS Power Requirements:	2.56 kWatts

* *0.058 seconds in each stack*

MCFC Calculations

The MCFC calculations for stack size are outlined in the following manner. A current density of 160 mA/cm^2 was assumed. Processing of a synthesis gas stream which is 29.8 vol% H_2, 41.0 vol% CO, and 17.1 vol% H_2O at an 80% fuel utilization gives 76 gmole/sec of fuel oxidized. With two faradays of electricity produced for each mole of fuel utilized, this translates to 1.47 x 10^7 Amps of electricity produced. With a current density of 0.160 Amps/cm^2, the total area of the MCFC stack is 9.181 x 10^7 cm^2 (or 9.884 x 10^4 ft^2). At a cross cell potential of around 1 volt, this translates to a power production of 14700 kWatts. Thus, the EMS is only 4.2% the size of the MCFC for a 10MM SCFD treating facility and consumes only 0.02% of the power produced. If the individual cells in the stack are 4 ft wide and 6 ft long, there are 4118 individual cells in the stack.

If the fuel flow is divided evenly between each cell in the stack, the molar flowrate to each cell is only 4.915×10^{-2} gmole/sec. There are assumed to be 0.3 cm by 0.15 cm parallel flow channels across the surface of the electrodes. Thus, with the flow to each cell evenly divided into each flow channel, the molar flowrate through each channel is only 8.015×10^{-5} gmole/sec. This translates to a volumetric flow of 6.07 cm^3/sec. The gas velocity in each channel is therefore 1.35 meters/sec. This gives a residence time in the stack of 1.38 seconds and a Reynold's Number of 24.

A summary of the MCFC design calculations results follows in Table 3.

Table 3.
Summary of MCFC Design Calculations

Current Density:	160 mA/cm^2
Total Current in Stack:	1.47×10^7 Amps
Total Stack Area:	9.88×10^4 ft^2
Individual 4 ft by 6 ft Cells in Stack:	4118
Gas Velocity in Each Flow Channel:	1.35 m/sec
Cell Residence Time:	1.36 seconds
Reynold's Number:	24
MCFC Power Production:	14700 kWatts

Experimental Results

To date, five experimental runs of the laboratory scale EMS unit here at Georgia Tech have attempted to verify the polishing applications of this technology with simulated coal gasification product streams. The gas used in these experiments had an initial composition of approximately 18.0% CO_2, 38.0% H_2, 44.0% CO, and 100 ppm H_2S.

The cell housings were either made from 316 stainless steel or MACOR machinable ceramic blocks. The housings were 3" diameter, 1" thick cylinders with gas flow channels machined into the large surface faces. Gas flow tubes were connected to supply process and sweep gases to the cell (see Figure 2). Once the electrode and membrane materials were ready for testing, the electrodes were either set onto platinum current collectors if the MACOR housings were used, or directly onto the steel flow channels if the 316 SS housings were used (the SS housings acted as their own current collectors). The electrodes contacted the gas stream on one side and the electrolyte membrane on the other (see Figure 2). The full cell was then assembled by placing the membrane between the housing blocks and connecting the gas supply lines to the assembly.

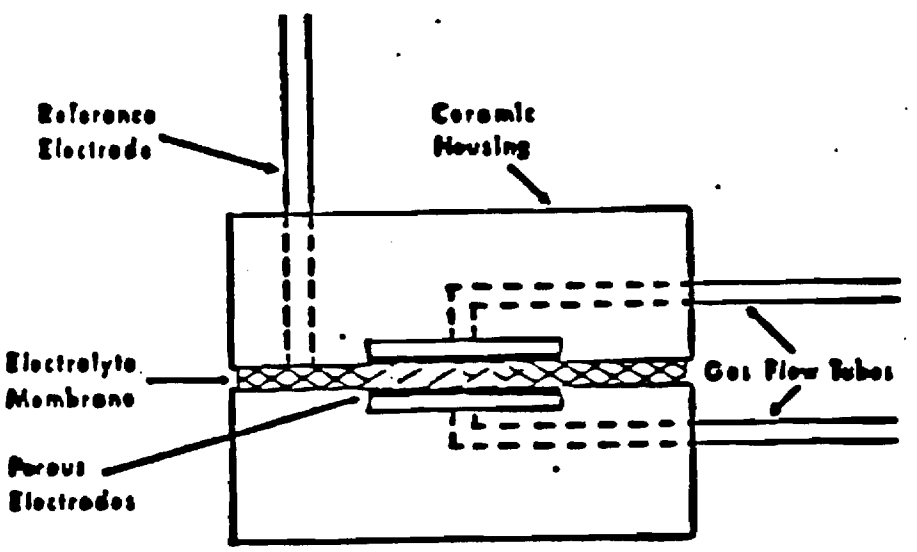

Figure 2.
Experimental Cell Configuration.

When current is applied to the electrochemical cell, H_2S is reduced at the cathode:

$$H_2S + 2\ e^- \rightarrow H_2 + S^{2-} \tag{1}$$

However, carbon dioxide and water vapor compete in the reduction reaction by:

$$CO_2 + H_2O + 2\ e^- \rightarrow CO_3^{2-} + H_2 \tag{11}$$

If hydrogen is present at the anode, then the following oxidation reactions occur after transport of the ionic species through the membrane:

$$S^{2-} + H_2 \rightarrow H_2S + 2\ e^- \tag{12}$$

$$CO_3^{2-} + H_2 \rightarrow CO_2 + H_2O + 2\ e^- \tag{13}$$

By summing the half-cell reactions for sulfide transport (1) and (12) and the half-cell reaction for carbonate transport (11) and (13) one can see that if H_2 is present at the anode there is no net cell reaction and species are concentrated on the anode side of the membrane. The ionic flux through the membrane in this case depends on the relative mobilities of carbonate and sulfide as well as the concentrations of H_2S and CO_2 (and H_2O) in the process gas. Since CO_2 and H_2O are present in orders of magnitude higher concentrations than H_2S, they are preferentially transported.

If no hydrogen is present at the anode, the following oxidation reactions take place:

$$S^{2-} \rightarrow \frac{1}{2} S_2 + 2\ e^- \tag{2}$$

and

$$CO_3^{2-} \rightarrow CO_2 + \frac{1}{2}O_2 + 2\ e^- \tag{14}$$

The direct oxidation of carbonate by reaction (14) takes place at a standard potential some 700 mV more positive than that for sulfide. When summed, the half-cell reactions for the transport of sulfide (1) and (2) at 900 K gives:

$$H_2S \rightarrow H_2 + \frac{1}{2} S_2 \qquad E^o = -0.239V \tag{15}$$

When the half-cell reactions for the transport of carbonate (11) and (14) are summed, the resulting cell reaction and standard potential are:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad E^o = -1.030V \tag{16}$$

This gives an electrochemical 'window of operation'. If no H_2 is present at the anode and if the cell potential is maintained below -0.239 V yet above -1.030 V, the net

effect is the continuous removal of H_2S from the process gas accompanied by enrichment of the process gas with H_2 and direct generation of elemental sulfur. This mode of operation is preferable for commercial application, with one-step removal of H_2S and direct production of elemental sulfur as a by-product. Actual experimental results are as follows:

Run 44

This was our first attempt at the application of this technology to coal synthesis gas H_2S separation. The membrane used in this experimental run was three of MgO tape casts layered together with the acrylic binder burned out in-situ under an O_2 atmosphere. Eutectic composition Li/K carbonate (62% Li, 38% K) was then wicked into the membrane in-situ. Both the anode and cathode were lithiated NiO.

The coal synthesis gas fed to the cell after binder burn-out and electrolyte impregnation had an initial composition of 18.0% CO_2, 38.0% H_2, 44.0% CO, and 100 ppm H_2S. After allowing for the water-gas shift reaction:

$$CO + H_2O = CO_2 + H_2 \tag{17}$$

$$K_a = \frac{(P_{CO_2} * P_{H_2})}{(P_{CO} * P_{H_2O})} \tag{18}$$

which has a K_a of 1.865 at 650° C, the composition of the gas in the cell was 13.2% CO_2, 33.2% H_2, 48.8% CO, 4.8% H_2O, and 100 ppm H_2S (assuming that the gas has gone to its equilibrium composition).

Using these gas compositions, the electrolyte equilibrium reaction:

$$(Li_{0.63}K_{0.38})_2CO_3 + H_2S \rightleftharpoons (Li_{0.62}K_{0.38})_2S + CO_2 + H_2O \tag{19}$$

$$K_a = \frac{(a_{M_2S} * P_{CO_2} * P_{H_2O})}{(a_{M_2CO_3} * P_{H_2S})} \tag{20}$$

was analyzed. K_a was found to be 3.57 at 650°C. This corresponded to an electrolyte equilibrium composition of 99.6% carbonate and 0.4% sulfide.

The run was terminated before any removal data was collected. Several factors contributed to the decision to terminate the experiment. First of all, the control relay on the furnace froze shut, causing the temperature to overshoot the acrylic burnout temperature of 350°C by over 300°. This damaged the membrane before the electrolyte was added and allowed process gas to cross over and mix with the sweep gas. The gas chromatograph results also became highly variable. It was found that a piece of the injection port septum broken off and fallen into the injection chamber, interfering with carrier gas flow. The GC was repaired and the run terminated due to gas cross-over through the damaged membrane.

The cell was shut down after 14.8 hrs of operation.

Run 45

This was the second attempt at polishing H_2S from coal gas, and the first using 316 stainless steel cell housings. The housings themselves acted as the current collectors with the galvanistat hooked directly onto the gas flow tubes. Aluminum foil gaskets were used to try to protect the stainless steel housings and improve gas seals by forming a protective layer of $LiAlO_2$ in-situ. The membrane was three MgO tapes layered together with the acrylic binders burned out in-situ and subsequently wetted with Li/K eutectic carbonate electrolyte. Both cathode and anode were lithiated NiO.

Initially, seals were excellent with both process gas and sweep gas pushing over 5 inches of H_2O back-pressure with no decrease in exit flow-rate. These seals were damaged, however, when the housings were adjusted in an effort to correct a current short between the cell housings.

No removal data was collected as the cell was shut down due to the current short across the cell. A post mortem examination of the cell showed a bead of what appeared to be molten aluminum shorting between the cathode housing and the anode housing. This is surprising considering the 'bead' was outside the cell housings and exposed to furnace air at 650°C. One would have expected such a 'bead' to oxidize to non-conductive Al_2O_3. However, if the bead was formed over an area of the cell where reducing fuel gas was leaking into the furnace, it may have been protected from oxidation.

The cell was shut down after 8.15 hrs of operation.

Run 46

This experimental run was the third attempt at polishing H_2S from coal gas. The cell used three MgO tapes layered together within the stainless steel housings. No aluminum gaskets were used. Both the cathode and the anode were NiO and the electrolyte was eutectic composition Li/K carbonate. No useful removal data was collected from the cell. The extremely low cross-cell potentials together with the fact that the cathodic to reference potential was positive suggests that cross-over was present even though none was observed directly. Very low cross-over flow will carry enough hydrogen to transport carbonate with essentially no cross-cell potential.

The cell was shut down after 24.1 hrs of operation.

Run 47

This was the fourth attempt at polishing H_2S from coal gas. The cell used two layers of MgO tape with a mat of zirconia woven cloth from Zircar, Inc. for strength. The stainless steel cell housings were used with smaller aluminum foil gaskets around the wet seal area. These smaller gaskets had an outer diameter of only two inches and an inner diameter of 1.5 inches. This put the inner and outer edge of the gasket well away from either the edge of the electrode or the outer edge of the membrane. This was done to prevent a current short from forming as in run 45. The electrolyte was eutectic Li/K carbonate and the electrodes were both lithiated NiO.

The cell survived an initial temperature overshoot during the acrylic burn-out stage when the furnace control relay froze shut and ran the cell temperature up to

750°C. The zirconia mat gave enough re-enforcement to the membrane to allow it to survive this shock. The electrolyte was added after the cell had cooled back down to the run temperature of 650°C.

A small effect of current was observed after 18.8 hours with 3mA (0.37 mA/cm^2) applied to the cell. This current level should have been sufficient for 155% removal of H_2S from the process gas stream assuming that all the current was carried by the sulfide ion. Only 26.4% removal was observed (exit H_2S concentration dropping from 31.3 ppm to 23.1 ppm at 150 cc/min total gas flowrate). An alternative, parallel current path was suspected. This seemed to be verified by the fact that the cell could still conduct current even after it had cooled to below the melting temperature of the electrolyte (R = approx. 4 MΩ). At run temperatures, this alternative current path could act in parallel with ion transport, cutting down the cell's current efficiency.

The cell was shut down after 152.7 hrs of operation.

Run 48

This experimental run was the fourth run using coal gas and, like the previous run, used two tapes of MgO and one mat of zirconia cloth as the membrane matrix material. The electrodes were both lithiated NiO. The acrylic binders were burned out under an O_2 atmosphere and the Li/K eutectic composition electrolyte was added with the cell at run temperature. MACOR machinable ceramic housings were used instead of the stainless steel housings and the inlet gas steam was hydrated to a level of 3.3% H_2O by passing the simulated coal gas through a bubbler since the cell did

not have a shift reactor in the gas line before the cell to allow the CO_2 and H_2 to go to an equilibrium H_2O and CO levels through the water-gas shift reaction.

CO_2 removal from the process gas as a function of applied current was recorded and is presented in Table 4. Examination of this data shows that the removal of CO_2 from the cathode side of the cell and production of CO_2 at the anode side of the cell is stoichiometric across the range of applied currents examined.

Cell seals were initially excellent on both sides of the cell, but flow out the anode side of the cell eventually stopped. Shortly after the anode flow stopped, cell cross-flow was observed and the cell run was terminated.

The cell run was terminated after 6.75 hours.

Table 4.
Run 48 Recorded Data.

Applied Current (mA)	Actual Cathode CO_2 Out	Calc. Cathode CO_2 Out	Actual Anode CO_2 Out	Calc. Anode CO_2 Out
0	19.0 %	19.0 %	0.0 %	0.0 %
100	18.4 %	18.6 %	0.6 %	0.8 %
200	18.2 %	18.1 %	1.2 %	1.5 %
300	18.2 %	17.7 %	2.0 %	2.3 %
400	17.2 %	17.2 %	2.7 %	3.1 %
500	16.8 %	16.8 %	3.7 %	3.8 %
600	15.6 %	16.3 %	4.2 %	4.6 %

Summary

Marginal success with the application of this removal cell to the polishing of H_2S from simulated coal gasification process streams has been shown. Some success has also been shown on the use of 316 stainless steel as a cell housing material for the coal gasification process gas polishing application. The CO_3^{2-} transport reactions were studies in coal gas and CO_2 removal was shown to be stoichiometric.

Planned Work for Next Quarter

Work will continue on the application of this technology to the polishing of coal gasification process streams. Use of Molten Carbonate Fuel Cell Materials (stainless steel housings, Ni/NiO electrodes, and eutectic Li/K carbonate electrolyte membranes) will be the main goal.

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2) Reid, R.C., Prausnitz, J.M., and Poling, B.E., The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York, 1987.

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Quarterly Progress Report:

High Temperature Electrochemical Separation of H_2S from Coal Gasification Process Streams

Grant DE-PS22-91PC91282

January 1, 1992 - March 31, 1992

by

Professor Jack Winnick

Georgia Institute of Technology

School of Chemical Engineering

Atlanta, Georgia 30332-0100

Purpose and Goals of Research

An advanced process for the separation of hydrogen sulfide from coal gasification product streams through an electrochemical membrane is being developed using the funds from this grant. H_2S is removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. The process allows removal of H_2S without cooling the gas stream and with negligible pressure loss through the separator. The process is economically attractive by the lack of adsorbents and the lack of a Claus process for sulfur recovery.

Research conducted during the present quarter is here highlighted, with an emphasis on progress towards the goal of an economically viable H_2S removal technology for use in coal gasification facilities providing polished fuel for co-generation coal fired electrical power facilities and Molten Carbonate Fuel Cell electrical power facilities.

Introduction

The process under development is presented schematically in Figure 1. The process gas, cleaned of particulates, is passed by the cathode. Here, the most easily reduced species will be electronated; under these conditions, it is H_2S:

$$H_2S + 2\,e^- \rightarrow S^{2-} + H_2 \tag{1}$$

The sulfide ions are maintained, with alkali-metal cations, as a fused electrolyte in a ceramic membrane. The sulfide is transported across to the anode, where it is oxidized to elemental sulfur. An inert gas such as N_2 is used at the anode to carry away the vaporous sulfur, S_2, to be condensed for recovery downstream.

$$S^{2-} \rightarrow \frac{1}{2}S_2 + 2\,e^- \tag{2}$$

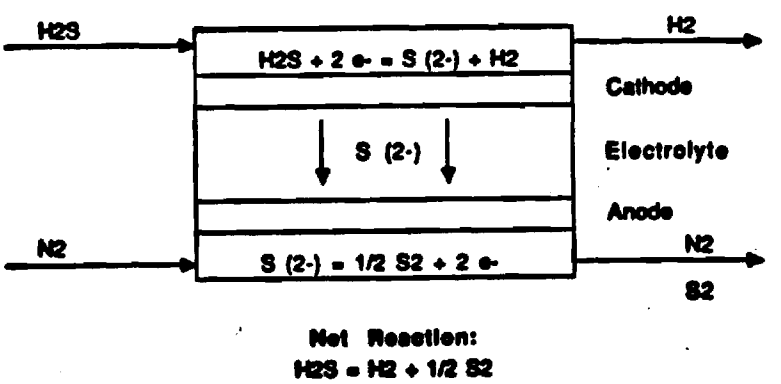

Figure 1.
Schematic of H_2S Removal Cell.

Theoretical Analysis

A theoretical analysis of cell electronic performance was performed in an attempt to model cross-cell potential as a function of cell H_2S removal (or applied current). This analysis proceeded in the following manner:

The minimum electrical work required to operate a separation cell at constant temperature and pressure is given by the change in Gibbs free energy (ΔG) of the electrochemical reaction:

$$W_{el} = \Delta G = -nFE \tag{3}$$

where n is the number of electrons transferred in the reaction, F is Faraday's constant (96500 coulombs/equivalent), and E is the reversible potential of the cell. If all the reactants and products are in the standard state, then

$$\Delta G^o = -nFE^o \tag{4}$$

If half-cell reactions (1) and (2) are summed, the overall cell reaction becomes:

$$H_2S \rightarrow H_2 + \frac{1}{2}S_2 \tag{5}$$

So, for this overall cell reaction, the free energy change can be expressed by the equation:

$$\Delta G = \Delta G^o + RT \ln\left(\frac{P_{H_2 Anode} P_{S_2 Anode}^{\frac{1}{2}} a_{S^{2-} Anolyte}}{P_{H_2S Cathode} a_{S^{2-} Catholyte}}\right) \tag{6}$$

When equations (6) and (7) are combined we have:

$$E = E^o + \frac{RT}{nF} \ln\left(\frac{P_{H_2 Anode} P_{S_2 Anode}^{\frac{1}{2}} a_{S^{2-} Anolyte}}{P_{H_2S Cathode} a_{S^{2-} Catholyte}}\right) \tag{7}$$

which is the form of the Nernst equation specific to this system.

Additional electrical work is required to run the separation cell because of irreversible losses. These losses originate primarily from three sources: (i) ohmic polarization (η_{ohm}), (ii) concentration polarization (η_{conc}), and (iii) activation polarization (η_{act}). These losses result in a cell voltage (V) which is greater then the reversible potential.[1]

Ohmic Polarization: The ohmic losses occur because of resistance to the flow of ions in the electrolyte and resistance to the flow of electrons through the electrode materials. Because both the electrolyte and the electrodes obey Ohm's law, the ohmic losses can be expressed by the equation:

$$\eta_{ohm} = IR \tag{8}$$

where I is the current flowing through the cell, and R is the total cell resistance, which includes electronic, ionic and contact resistances.

Concentration Polarization: As a reactant is rapidly consumed at the electrode by electrochemical reaction, concentration gradients are established. Several processes contribute to concentration polarization: slow diffusion in the gas phase in the electrode pores, solution/dissolution of reactants/products into/out of the electrolyte, of diffusion of reactants/products through the electrolyte to/from the electrochemical reaction site. At practical current densities, slow transport of reactants/products to/from the electrochemical reaction sites is a major contributor to concentration polarization.

The rate of mass transport to an electrode surface can be described by Fick's first law of diffusion

$$i = \frac{nFD(C_{H_2S_B} - C_{H_2S_S})}{\delta} \tag{9}$$

where D is the diffusion coefficient of the reacting species, $C_{H2S\,B}$ is the concentration of H_2S in the bulk, $C_{H2S\,S}$ is the concentration of H_2S at the electrode surface, and δ is the thickness of the diffusion layer. The limiting current (i_L) is the maximum rate at which reactant can be supplied to an electrode, and occurs when $C_{H2S\,S} = 0$:

$$i_L = \frac{nFD\,C_{H_2S_B}}{\delta} \tag{10}$$

By combining equations (9) and (10) we have:

$$\frac{C_{H_2S_S}}{C_{H_2S_B}} = 1 - \frac{i}{i_L} \tag{11}$$

The Nernst equation for the reactant species at equilibrium conditions, or when no

current is flowing, is:

$$E_{i=0} = E^{o} + \frac{RT}{nF} \ln C_{H_2S_B} \tag{12}$$

When current is applied, the surface concentration becomes less than the bulk concentration and the Nernst Equation becomes:

$$E = E^{o} + \frac{RT}{nF} \ln C_{H_2S_s} \tag{13}$$

the potential difference (ΔE) produced by a concentration change at the electrode is called the concentration polarization:

$$\Delta E = \eta_{conc} = \frac{RT}{nF} \ln\left(\frac{C_{H_2S_s}}{C_{H_2S_B}}\right) \tag{14}$$

By combining equations (11) and (14) we obtain the expression for concentration polarization in terms of applied current:

$$\eta_{conc} = \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right) \tag{15}$$

Activation Polarization: The activation polarization at the cathode and the anode of the cell is directly related to the rates of electrochemical reactions occurring at these electrodes. There is a close similarity between electrochemical and chemical reactions in that both involve an activation barrier that must be overcome by the reacting species. The standard model to describe the current-overpotential relationship behind

these electrochemical kinetics is the Butler-Volmer equation[2]:

$$i = i_o \left[\exp\left(\frac{\alpha_a F \, \eta_{act,electrode}}{RT}\right) - \exp\left(\frac{-\alpha_c F \, \eta_{act,electrode}}{RT}\right)\right] \tag{16}$$

This equations holds at a specified temperature, pressure, and concentration of reacting species. Since the electrochemical kinetics can be different at the cathode and anode of the cell, the electrochemical parameters α_a, α_c, and i_o must be determined for each electrode. Also, the transfer coefficients, α_a and α_c, sum to the number of electrodes transferred in the reaction:

$$\alpha_a + \alpha_c = n \tag{17}$$

Electrode Polarization: The total polarization at each electrode is the sum of the activation polarization ($\eta_{act,\ electrode}$) and the concentration polarization ($\eta_{conc,\ electrode}$):

$$\eta_{electrode} = \eta_{act,\ electrode} + \eta_{conc,\ electrode}$$

The effect of polarization is to shift the potential of the electrode ($E_{electrode}$) to a new value ($V_{electrode}$):

$$V_{electrode} = E_{electrode} \pm |\eta_{electrode}| \tag{19}$$

For the cathode:

$$V_{cathode} = E_{cathode} - |\eta_{cathode}| \tag{20}$$

and for the anode:

$$V_{anode} = E_{anode} + |\eta_{anode}| \tag{21}$$

Cell Voltage: The cell voltage includes the contribution of the polarization and the anode and cathode potentials:

$$V_{cell} = V_{cathode} - V_{anode} - IR \tag{22}$$

When equations (20) and (21) are substituted into equation (22) we have:

$$V_{cell} = \Delta E_e - |\eta_{cathode}| - |\eta_{anode}| - IR \tag{23}$$

with ΔE_e equal to $E_{cathode} - E_{anode}$.

The following data was generated using this model. The run conditions models consisted of equal cathodic and anodic flowrates (200 cc/min), a system pressure of 1 atmosphere, a run temperature of 625°C, and the polishing of H_2S from 100 ppm down to 10 ppm. The cathodic and anodic exchange current densities were estimated at 40 mA/cm^2 after the results of the free electrolyte study performed by Banks[3]. The exchange coefficients, α_a and α_c, were assumed to each be unity. Ohmic resistance across the cell was estimated to be only 1 Ω. The results of this model are presented in Table 1 and graphically in Figure 2.

Table 1.
Theoretical Cross-Cell Potentials

Removal	Nernst (V)	Ohmic (V)	Cat.Act.(V)	An. Act.(V)	Conc.(V)	Total(V)
10%	-0.081	-2.60E-4	-3.42E-5	3.42E-5	-0.004	-0.089
20%	-0.099	-5.20E-4	-6.85E-5	6.85E-5	-0.009	-0.117
30%	-0.112	-7.80E-4	-1.03E-4	1.03E-4	-0.014	-0.141
40%	-0.123	-1.04E-3	-1.37E-4	1.37E-4	-0.020	-0.165
50%	-0.135	-1.30E-3	-1.71E-4	1.71E-4	-0.027	-0.191
60%	-0.147	-1.56E-3	-2.05E-4	2.05E-4	-0.036	-0.221
70%	-0.162	-1.82E-3	-2.40E-4	2.40E-4	-0.047	-0.258
80%	-0.180	-2.08E-3	-2.74E-4	2.74E-4	-0.062	-0.308
90%	-0.209	-2.34E-3	-3.08E-4	3.08E-4	-0.089	-0.391

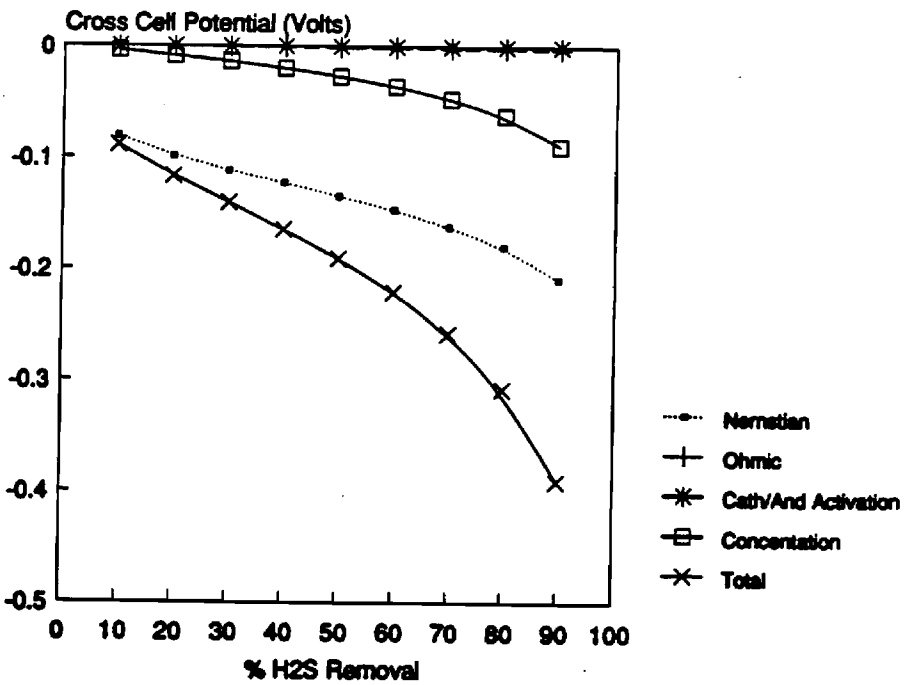

Figure 2.
Theoretical Cross Cell Potential vs % Removal.

Examination of this data shows that the activation polarization at both the cathode and the anode is negligible. This shows extremely rapid electrochemical kinetics when compared to diffusion effects in the gas phase and in the electrolyte. Actual exchange current densities in full removal cells will likely be smaller due to electrolyte wetting the pores of the electrodes, porosity, and tortuosity of the electrodes. However, activation polarizations at the electrodes are expected to remain negligible and the values used in this study represent an 'order-of-magnitude' estimate. All cross-cell potentials are shown to be primarily Nernstian and concentration polarization effects. Comparison of these results to the experimental cell results from Run 49C shows that as a rough estimate, they are correct.

Experimental Results

Seven experimental runs with simulated coal gasification product streams were attempted this quarter (Runs 49 through 55). Run 49 showed successful removal of H_2S as a function of applied current. Runs 50 through 55 were not successful. A summary of these experiments follows:

Successful Runs

Run 49

This experimental run used one mat of ZYW-30A zirconia cloth layered two tapes of MgO as the matrix material and Li/K eutectic carbonate electrolyte. The electrolyte was allowed to go to its equilibrium sulfide concentration in-situ. MACOR

machinable ceramic housings were used the gases were run through a stainless steel shift reactor to allow them to go to their equilibrium composition before entering the cell. The electrodes were both lithiated NiO.

The run was divided into three sections: the first confirmed ionic transport through the membrane by removal of CO_2 (and H_2O) from the syn-gas at 625°C (Run 49A), the second was an attempt at removal of H_2S from the syn-gas at 625°C (Run 49B), and the third was an attempt at removal of H_2S from the syn-gas at 700°C (Run 49C). The results of these studies follow:

Run 49A

CO_2 removal from the process gas as a function of applied current was recorded. Successful removal of CO_2 (and H_2O) with current showed that the cell was functioning properly with respect to ionic transport. At the cathode, CO_2 and H_2O combine to form CO_3^{2-} and H_2:

$$CO_2 + H_2O + 2e^- \rightarrow CO_3^{2-} + H_2 \tag{24}$$

At the anode, CO_3^{2-} goes to CO_2 and O_2:

$$CO_3^{2-} \rightarrow CO_2 + \frac{1}{2}O_2 \tag{25}$$

The recorded data is presented in Table 2.

Table 2.
Run 49A Recorded Data.

Applied Current (mA)	Actual Cathode CO_2 Out	Calc. Cathode CO_2 Out	Actual Anode CO_2 Out	Calc. Anode CO_2 Out
0	17.8%	17.8%	0.0%	0.0%
100	16.8%	16.8%	1.8%	1.2%
200	15.8%	15.7%	2.8%	2.4%
300	15.2%	14.7%	3.8%	3.7%

This data shows that the cell was functioning properly with respect to ionic transport of carbonate through the electrolyte. The fuel gas flow was set at 75 cc/min and the N_2 sweep was set at 63 cc/min.

Run 49B

No current effect on H_2S was observed after 27.7 hours with an applied current density of 0.63 mA/cm^2. Examination of the limiting current densities at this run temperature shows that at 625°C the gas phase limiting current density was only 1.1 mA/cm^2 while the membrane limiting current density was only 1.4 mA/cm^2. This membrane limiting current density assumes that the electrolyte diffusivity was 10^{-5} cm^2/sec. Once membrane porosity and tortuosity are taken into account, this estimate is in all probability too large. As an 'order-of-magnitude' estimate, however, it does show that the transport through the membrane is on the same order as the transport through the gas phase. It is probable that at these temperatures, the membrane cannot support the necessary flux of sulfide ion to significantly affect the exit H_2S concentration.

Run 49 C

At 700°C, analysis of the limiting current densities within the system showed that the gas phase limiting current density was 1.2 mA/cm^2 while the membrane limiting current density was 3.3 mA/cm^2. This shows that even if the electrolyte diffusivity estimate is in error, the membrane flux is three times greater than at 625°C. H_2S removal at a variety of flow rates was observed and is presented in Figure 3. Overpotentials as a function of applied current and flowrate are presented in Figure 4. The lowest level to which H_2S was driven was 9.7 ppm (89.1% removal, zero current basis). This data shows good response of the system to applied current. The overpotentials required to accomplish this removal are negligible.

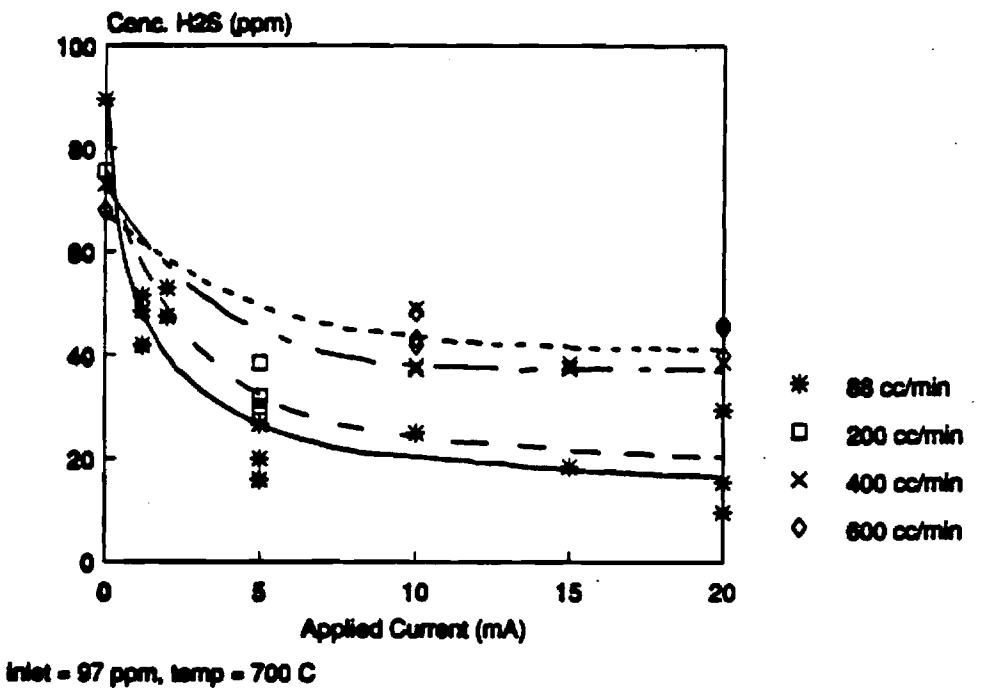

Figure 3.
H_2S Removal versus Applied Current and Flow Rate, Run 49C.

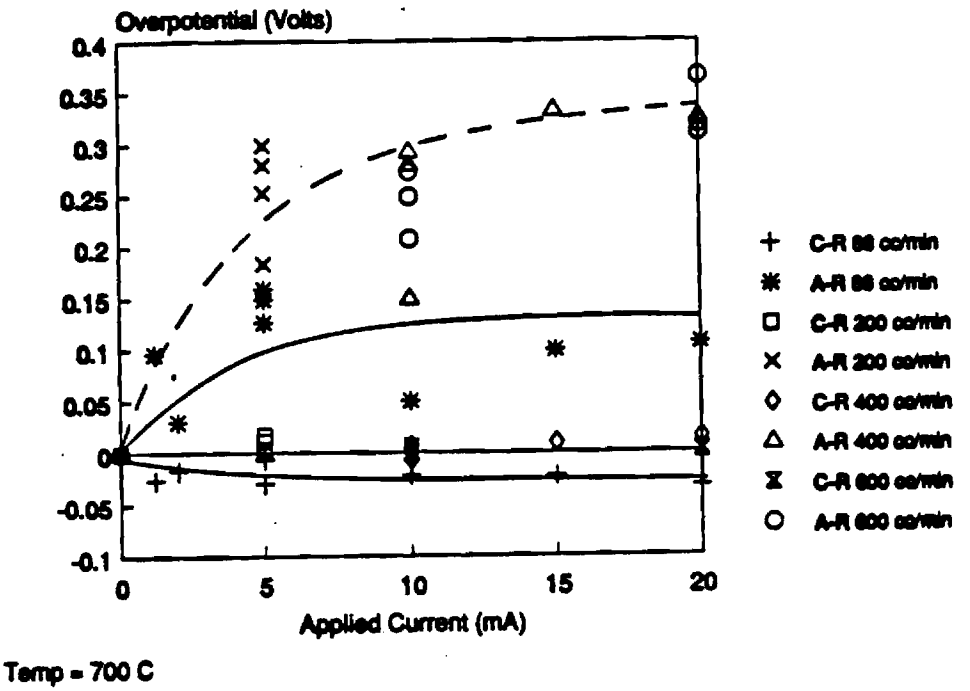

Figure 4.
Overpotential versus Applied Current and Flow Rate, Run 49C.

Unsuccessful Runs

Runs 50 through 55

After run 49, the cell housings were changed to type 316 stainless steel in an attempt to simulate an actual membrane separator configuration in an industrial environment. Runs 50 through 55 are outlined as follows:

Run 50

A 20 micron thick coating of Al was sputtered onto the wet contact surfaces. This Al coating would be converted in-situ to $LiAlO_2$ by reactions with the Li_2CO_3 in the electrolyte[4]. The electrodes were lithiated NiO and the membrane was two tapes of MgO layered with two mats of ZYW-30A. The membrane was damaged at start-up

by adding molten electrolyte through the reference electrode hole on the cathode side of the cell. It appears that the density change caused by absorbing the electrolyte had damaged the membrane. The cell was shut down due to uncontrollable cross-flow.

Run 51

The stainless steel housings of this run were painted with 29 wt% Al paint. The electrodes were both lithiated Ni and were allowed to go to NiO in-situ. The membrane was two tapes of MgO layered with one mat of ZYW-30A and the electrolyte was added by pressing the amount required to saturate the matrix material into a disk and layering it within the membrane at start-up. Once the electrolyte melted cell seals were good and the system responded well to CO_2 removal. Cross cell electronic resistance was high (R=1.4 Ω), however, and two more grams of electrolyte were added. This excess electrolyte ran into the exit anode tube and froze, clogging the tube and rupturing the membrane with the subsequent pressure build-up. The cell was shut down because the membrane was destroyed.

Run 52

This experimental run was identical to run 51. It also was shut down due to excess electrolyte flooding the anode side of the cell and clogging the anode exit tube. In this case, however, the anode seal blew out before the membrane ruptured. The cell was cooled of and the anode exit line was replaced. On heating back up to run

temperature, the anode exit tube became clogged once again. The cell membrane did not survive this second temperature cycle as the best current efficiency that could be observed for CO_2 removal was only 30%. Hydrogen cross-over and CO_2 back diffusion were present at sufficient levels to offer no hope for successful H_2S removal. The cell was shut down for this reason.

Run 53

The set-up for this run was identical to the set-up for the previous two runs. The run was heated all the way to run temperature under O_2. This caused the electrolyte to decompose by the following reaction:

$$(Li_{0.62}K_{0.38})_2CO_3 \rightarrow (Li_{0.62}K_{0.38})_2O + CO_2 \qquad (26)$$

By analysis of this reaction at the run temperature of 700°C, at least 300 ppm CO_2 would have to be present in the cathode and anode streams to prevent this decomposition of the electrolyte. The cell was shut down because decomposition of the electrolyte led to membrane failure.

Run 54

This experimental run was used as a training run for the new graduate student. The set-up was identical to the previous run. Leaks in the tubes connecting the manometer across the cathode and the anode sides of the cell lead the student to believe that the membrane had blown and that there was bulk mixing of the process and sweep gas streams since no pressure difference across the membrane could be

detected when flow on either side of the cell was throttled. The cell was therefore shut down.

Run 55

The housings used in this experimental run were identical to the housings used in the previous experimental runs. Set-up was also identical, except that O_2 was only applied during the binder burn-out period. Once the cell had reached 350°C and had stayed at this temperature for 1 hour, fuel gas was started to the cathode side of the cell and N_2 to the sweep side of the cell. Temperature was then allowed to go to the run temperature of 700°C. This prevented the electrolyte decomposition seen in run 53. Once the cell had reached temperature, the cathodic CO_2 removal rate was observed to be close to 100%. However, the anodic production rate of CO_2 was less than 100%. This means that there was an alternative oxidation reaction taking place at the anode. Since the housings were acting as the current collectors, if the AL coating on the anode did not go to a homogeneous layer of $LiAlO_2$ and thus insulate the housing wet seal area, it is possible that electrolyte which had seeped out into the wet seal area was being oxidized:

$$CO_3^{2-} \rightarrow CO_2 + \frac{1}{2}O_2 + 2e^- \qquad (27)$$

CO_2 from electrolyte oxidized in the wet seal area could escape to the furnace and would not be detected in the anode exit stream.

Once cathodic removal efficiency had been determined, H_2S was started to the

cell at a level of 122 ppm. Some current effect on H_2S was observed (cathode exit H_2S level of 35 ppm with no current applied dropped to a level of 28 ppm with 200% stoichiometric current applied). However, the shift reactor, which allows the simulated fuel gas to reach its equilibrium composition through the water/gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{28}$$

began to clog with carbon. The reverse of the coal gasification reaction could occur at these conditions if the water level in the gas is too low:

$$CO + H_2 \rightleftharpoons C + H_2O \tag{29}$$

It seems that this reaction was happening before the water/gas shift reaction could build up enough water vapor to prevent the carbon monoxide decomposition reaction from depositing carbon in the shift reactor. This problem was corrected by burning the carbon out of the shift reactor with an air stream. Unfortunately, seal integrity was lost on the cathode side of the cell during this process. Seals became so bad that all gas entering the cathode side of the cell was blown into the furnace and ignited. No gas analysis could be performed on the cathode exit gases. The ignited gases raised the cell housing temperature locally which lead to aggressive electrolyte corrosion of the wet seal area. The cell was shut down to progressive corrosion of the cathode cell housing and loss of seal integrity. Carbon deposition can be prevented in future runs by hydrating the gas stream before it enters the shift reactor.

Summary

Polishing application of this technology to coal gasification synthesis gas has been demonstrated with H_2S removals as high as 89.1% recorded (Run 49C). No successful runs with stainless steel housings have yet been achieved. However, since stoichiometric CO_2 removal with stainless steel housings has been achieved, H_2S removal is achievable.

Planned Work for Next Quarter

Work with the stainless steel housings will continue. Since the key to successful use of stainless steel seems to be insulating the wet seal area, this will be accomplished by forming an intimately bound layer of Al metal on the wet seal surfaces and then allowing the Al to go to the non-conductive and protective $LiAlO_2$ in-situ.

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1) U.S. Dept. of Energy, Fuel Cells: A Handbook, DOE/METC-88/6090, Morgantown, West Virginia, 1988.

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3) Banks, E., and Winnick, J., *J. Appl. Electrochem.*, **16**, 1986.

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OMB Approval
No. 1910-1400

U. S. DEPARTMENT OF ENERGY

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     - Title of conference _____
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Quarterly Progress Report:

High Temperature Electrochemical Separation of H_2S from Coal Gasification Process Streams

Grant DE-PS22-91PC91282

April 1, 1992 - June 30, 1992

by

Professor Jack Winnick

Georgia Institute of Technology

School of Chemical Engineering

Atlanta, Georgia 30332-0100

Purpose and Goals of Research

An advanced process for the separation of hydrogen sulfide from coal gasification product streams through an electrochemical membrane is being developed using the funds from this grant. H_2S is removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. The process allows removal of H_2S without cooling the gas stream and with negligible pressure loss through the separator. The process is economically attractive by the lack of adsorbents and the lack of a Claus process for sulfur recovery.

Research conducted during the present quarter is here highlighted, with an emphasis on progress towards the goal of an economically viable H_2S removal technology for use in coal gasification facilities providing polished fuel for co-generation coal fired electrical power facilities and Molten Carbonate Fuel Cell electrical power facilities.

Introduction

The process under development is presented schematically in Figure 1. The process gas, cleaned of particulates, is passed by the cathode. Here, the most easily reduced species will be electronated; under these conditions, it is H_2S:

$$H_2S + 2\ e^- \rightarrow S^{2-} + H_2 \tag{1}$$

The sulfide ions are maintained, with alkali-metal cations, as a fused electrolyte in a ceramic membrane. The sulfide is transported across to the anode, where it is oxidized to elemental sulfur. An inert gas such as N_2 is used at the anode to carry away the vaporous sulfur, S_2, to be condensed for recovery downstream.

$$S^{2-} \rightarrow \frac{1}{2}S_2 + 2\ e^- \tag{2}$$

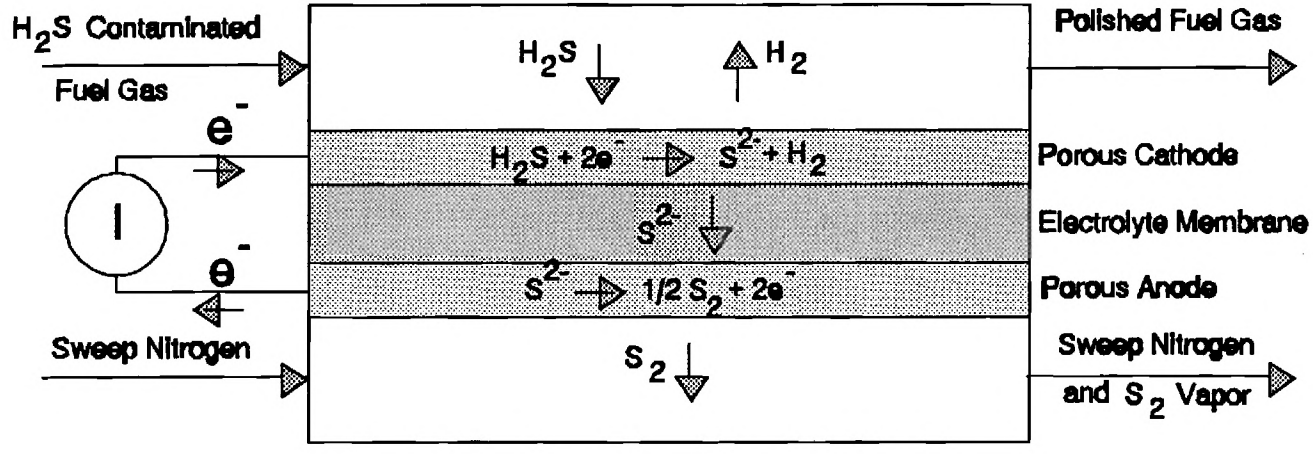


Figure 1. Schematic of H_2S Removal Cell.

Theoretical Analysis

A theoretical analysis of the cell electronic performance for H_2S removal was performed during the previous quarter (January 1, 1992 - March 31, 1992) which modeled cross-cell potential in the removal cell as a function of applied current. Two amendments to the results reported in the report covering this period are needed. First, the calculation of Nernstian effects on the cross cell potential need to be revised. The results reported in the 1/1/92 to 3/31/92 report used gas phase concentrations in units of parts-per-million in the calculation of H_2S. A more precise estimate is afforded by using gas phase mole fractions in the natural log term of the Nernst equation:

$$E = E^{o} - \frac{RT}{nF}\ln\left(\frac{P_{H_2 cathode} P_{S_2}^{\frac{1}{2}} {}_{Anode} a_{S^{2-}} {}_{Anode}}{P_{H_2S} {}_{Cathode} a_{S^{2-}} {}_{Cathode}}\right) \tag{3}$$

Revised estimates of cross cell potentials for this model are listed in Table I and presented graphically in Figure 2.

The data presented in Table I and Figure 2 were generated using equal cathodic and anodic flow rates (200 cc/min), a system pressure of 1 atmosphere, a run temperature of 625°C, and polishing H_2S from 100 ppm down to 10 ppm. Other gas phase components consisted of 13.3% CO_2, 33.2% H_2S, 48.8% CO, and 4.8% H_2O.

Examination of the data presented in Table I and Figure 2 shows that at 90%

Table I. Predicted Cross Cell Potential vs H_2S Removal (Revised).

Removal	Nernstian Potential	Ohmic Effect	Cathode Activation	Anode Activation	Concentration Polarization	Total (V)
10%	-0.350	-2.60E-4	-3.42E-5	3.42E-5	-0.004	-0.359
20%	-0.368	-5.20E-4	-6.85E-5	6.85E-5	-0.009	-0.386
30%	-0.382	-7.80E-4	-1.03E-4	1.03E-4	-0.014	-0.410
40%	-0.393	-1.04E-3	-1.37E-4	1.37E-4	-0.020	-0.434
50%	-0.404	-1.30E-3	-1.71E-4	1.71E-4	-0.027	-0.460
60%	-0.417	-1.56E-3	-2.05E-4	2.05E-4	-0.036	-0.490
70%	-0.431	-1.82E-3	-2.40E-4	2.40E-4	-0.047	-0.527
80%	-0.450	-2.08E-3	-2.74E-4	2.74E-4	-0.062	-0.577
90%	-0.479	-2.34E-3	-3.08E-4	3.08E-4	-0.089	-0.660

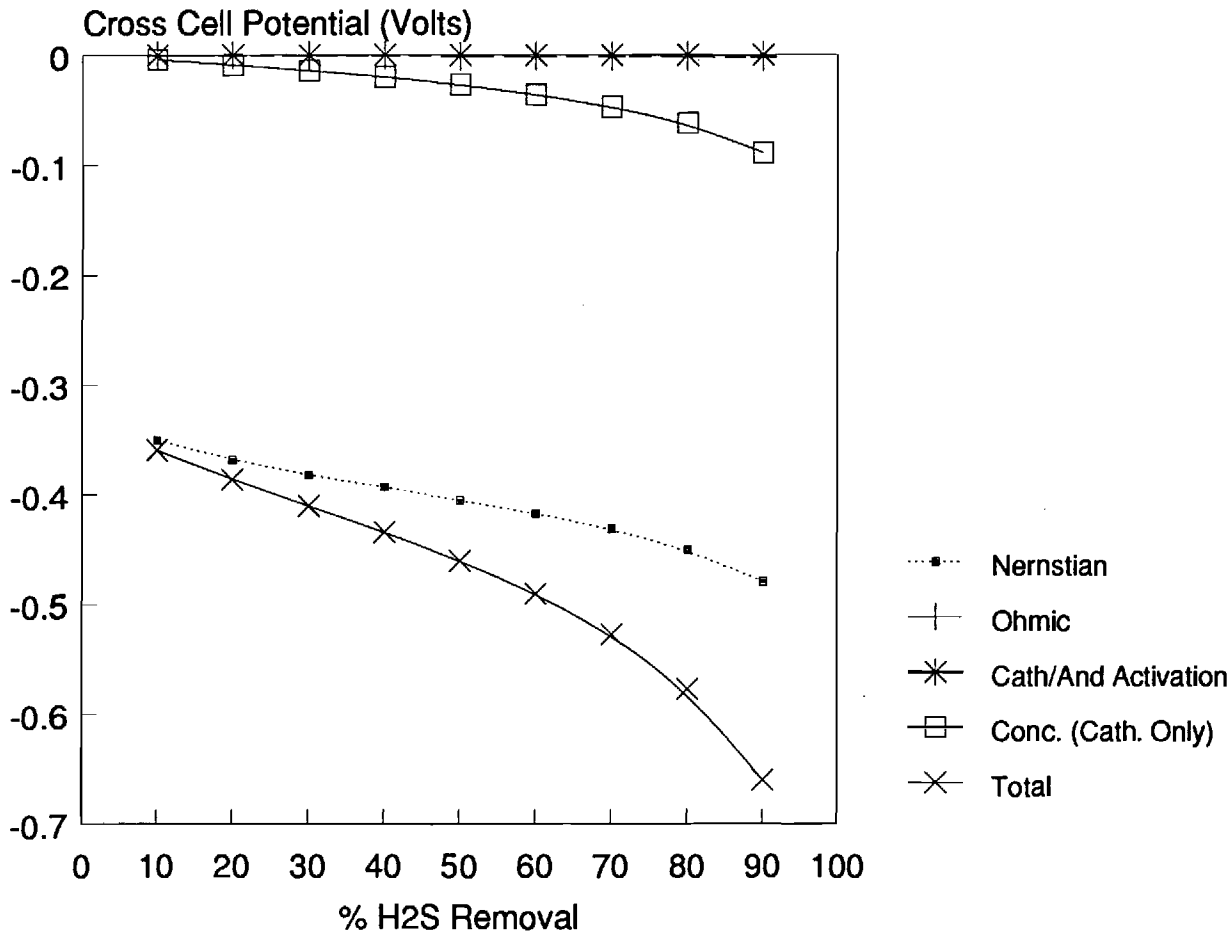


Figure 2. Theoretical Cross Cell Potential vs % H_2S Removal (Revised).

removal (100 ppm H_2S going to 10 ppm H_2S), a total cross cell potential of only about -0.660 V (cathode to anode) is expected.

Carbonate can also be electrochemically transported across the cell. At the cathode we have:

$$CO_2 + H_2O + 2e^- \rightarrow CO_3^{2-} + H_2 \tag{4}$$

and at the anode we have:

$$CO_3^{2-} \rightarrow CO_2 + \frac{1}{2}O_2 \tag{5}$$

The sum of these two half cell reactions and the standard cross-cell potential at 900 K is:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad E^o = -1.03\ V \tag{6}$$

The Nernst equation predicting the potential of this reaction as a function of product and reagent concentration is:

$$E = E^o - \frac{RT}{nF}\ln\left(\frac{P_{CO_2 anode} P_{O_2 anode}^{\frac{1}{2}} P_{H_2 cathode} a_{CO_3^{2-} cathode}}{P_{CO_2 cathode} P_{H_2O cathode} a_{CO_3^{2-} anode}}\right) \tag{7}$$

If reactions (1) and (2) are summed the total cell reaction and standard cross cell potential are:

$$H_2S \rightarrow H_2 + \frac{1}{2}S_2 \qquad E^o = -0.239\ V \tag{8}$$

Since the carbonate transport reaction (6) is parallel to the sulfide transport reaction (8), some current to the cell will also act to transport CO_2 across the cell. This means that there is a finite maximum current efficiency with respect to H_2S removal for any given H_2S removal, depending on gas composition and the cross-cell potential required for the desired separation of H_2S. By solving the Nernst equation for carbonate transport (7) at a given cross cell potential for the CO_2, H_2O and H_2 levels in the cathode gas and CO_2 and O_2 levels in the anode gas, the extent of this parallel reaction can be determined. This assumes that the electrode kinetics for sulfide and carbonate transport are equivalent (both contributing negligible activation overpotential) and that concentration overpotential for CO_2 removal is also negligible (a reasonable assumption since in this case study the concentration in some two to three orders-of-magnitude higher for CO_2 and H_2O than for H_2S. The extent of the anode CO_2 production with % H_2S removal is presented in Table II and Figure 3. Examination of this data shows that current efficiency drops to 34.9% at 90% H_2S removal. This means that applied current to the cell must be increased by a factor of 2.86 over stoichiometric current to achieve this removal level. The excess current goes to production of anodic CO_2. Thus, a total of 0.845 milliWatts/cm^2 of electrical

Table II. Predicted Anodic CO_2 Production and Maximum Current Efficiency vs H_2S Removal

Removal	Total Cell Potential (V)	Anode CO_2 (ppm)	Maximum Efficiency
10%	-0.359	0.95	93.0%
20%	-0.386	1.52	92.9%
30%	-0.410	2.29	92.9%
40%	-0.434	3.46	92.0%
50%	-0.460	5.40	90.2%
60%	-0.490	9.05	86.9%
70%	-0.527	17.1	80.4%
80%	-0.577	40.3	66.5%
90%	-0.660	168	34.9%

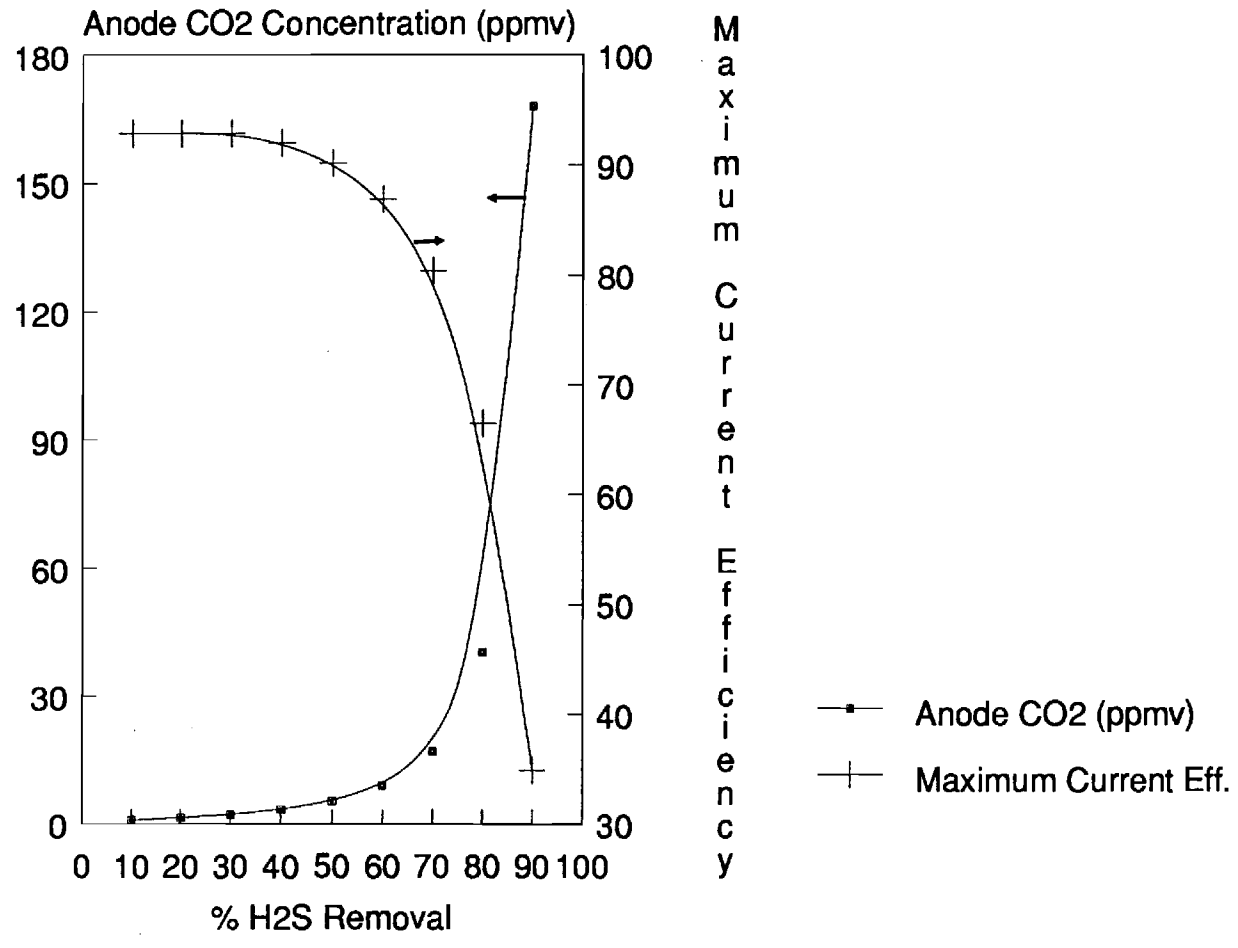


Figure 3. Predicted Anodic CO_2 Production and Maximum Current Efficiency vs H_2S Removal

power are actually required with 0.296 milliWatts/cm^2 going to H_2S removal. Even with a current efficiency of only 34.9%, power costs to perform this removal are negligible.

Research Summary

Work has continued on application of this technology to polishing H_2S from simulated coal gasification process streams. Both stainless steel and MACOR housings were successfully used, with 98% (100 ppmv H_2S to 2 ppmv H_2S) removal observed at a flow rate of 230 cc/min and a process temperature of 700°C with stainless steel housings (Run 57) and greater than 80% (11 ppmv H_2S to less than 2 ppmv H_2S) at a flow rate of 100 cc/min and a temperature of 650°C with MACOR housings (Run 65). Work has continued with attempts to increase removal efficiency by increasing the density of the membrane and slowing down H_2 diffusion from the cathode side to the anode side of the cell.

Experimental Run Results

Successful Runs

Run 56

This experiment used lithiated Ni as both the cathode and the anode of the cell. The membrane was two tapes of MgO suspended within an acrylic binder layered with two mats of zirconia cloth. This was layered with a pressed electrolyte

disk which used hydroxyethyl cellulose (HEC) as a binder material. These electrodes and membrane were loaded into a set of new 316 stainless steel housings which were painted with aluminum paint.

The cell was then heated to the binder burnout temperature of 350°C under pure O_2 at a rate of 200°C per hour. Once at the burnout temperature, N_2 was started to the cell and the cell was heated to 420°C. At this temperature, fuel gas (14.5% CO_2, 46.5% CO, 34.3% H_2, 6.1% H_2O, and 106 ppm H_2S after shift reaction at run temperature of 700°C) was started to the cell and the furnace was heated to 700°C. Under these conditions, the equilibrium sulfide level in the membrane should have been 0.6 mole%. The gas phase limiting current density was calculated as 1.22 mA/cm^2 and the membrane limiting current density was estimated as 1.87 mA/cm^2.

H_2S removal data (presented in Figure 4 and Table III) and cross-cell potential data (presented in Table III) were recorded. While some H_2S removal was recorded, current efficiencies were unacceptably low (with stoichiometric current at this concentration an flow rate being only 3 mA applied current). Current efficiency was low due to H_2 cross-over and the presence of a possible alternative current path.

After cell shut-down, carbon build-up between the electrodes in the membrane was observed. This may have been caused by pyrolized HEC since this was not observed in runs which did not use HEC as an electrolyte binder.

Run 57

Both electrodes in this experiment were lithiated Ni. The membrane was two

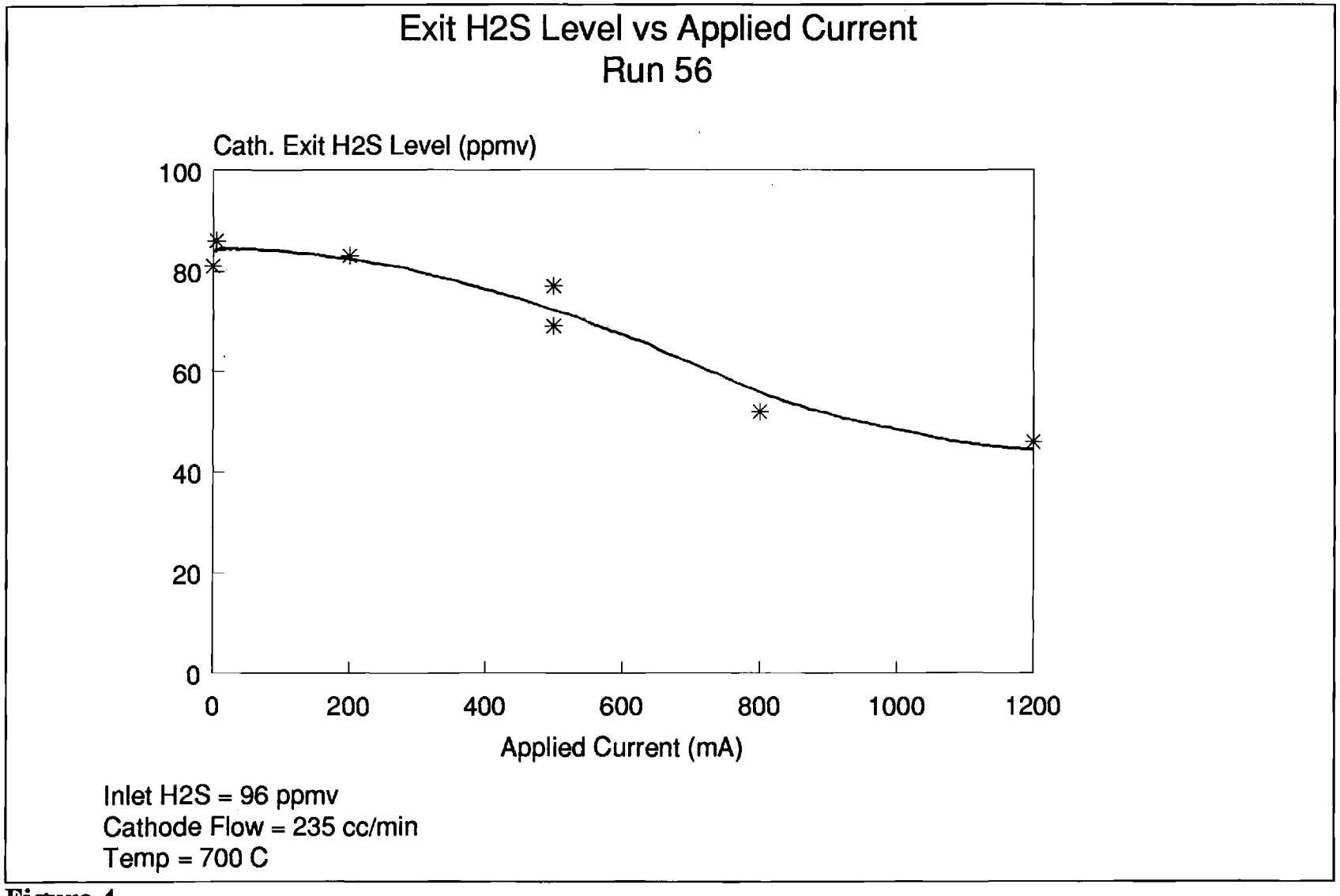

Exit H2S Level vs Applied Current
Run 56
Cath. Exit H2S Level (ppmv)
100
80
60
40
20
0
0
200
400
600
800
1000
1200
Applied Current (mA)
Inlet H2S = 96 ppmv
Cathode Flow = 235 cc/min
Temp = 700 C

Figure 4

Table III. Run 56 Data.

Run 56
Cathode = lithiated Ni Anode = lithiated Ni
Membrane = two tape casts of MgO layered with two mats of ZYW-30A (zirconia cloth)
Electrolyte = 0.8 mole% sulfide in eutectic Li/K carbonate pressed with HEC binder
Housings = type 316 SS with Al paint coating

Inlet Gas Composition = 96 ppm H_2S
18% CO_2, 45% CO, Balance H_2 (dry comp., before shift reaction)
Hydrated to 3.1% H_2O (before shift reaction)
Cathode Flow = 235 cc/min Anode Flow = 50 cc/min
Run Temp = 700°C

I_{app} (mA)	E_{C-A} (Volts)	Cath Exit H_2S (ppm)
0	-0.047	81.0
5	-0.039	86.0
200	-0.390	83.0
500	-0.739	77.0
500	-0.808	69.0
800	-1.598	52.0
1200	-2.020	46.0

tapes of MgO with two mats of zirconia cloth. One of the zirconia mats was cut with a wick extending out of the cell and resting in an electrolyte reservoir. This was to provide a continuous supply of electrolyte to the membrane in the event of electrolyte evaporation/reaction with the cell materials. The electrolyte loaded into the cell was 0.8 mole% sulfide in a carbonate supporting electrolyte. Eutectic carbonate electrolyte was loaded into the reservoir. The cell housings were 316 stainless steel painted with aluminum.

After binder burn-out and the cell had reached run temperature, fuel gas of final composition 14.4%CO_2, 45.1% CO, 6.2% H_2O, 34.2% H_2, and 113 ppmv H_2S was fed to the cell. This gives an equilibrium sulfide level in the electrolyte of 0.63 mole% sulfide. The gas phase limiting current density under these conditions was estimated to be 1.28 mA/cm^2 and the membrane limiting current density was estimated at 1.97 mA/cm^2.

H_2S removal data (presented in Figure 5 and Table IV). Removal of H_2S below 2 ppmv (GC detector limit) was recorded with only 5 mA (0.63 mA/cm^2) applied to the cell and a cross cell potential of only -275 mV (cathode to anode). Upon shutting off applied current, exit H_2S levels only returned to 24 ppm (113 ppm entering the cell). The electrolyte reservoir was removed since it was a potential carbonate sink for reaction with H_2S in the gas. Cell cross flow started soon after this and the cell was shut down. Apparently, electrolyte was wicked out of the membrane onto the surface of the steel housings thereby depleting the membrane of electrolyte and allowing gas cross-over.

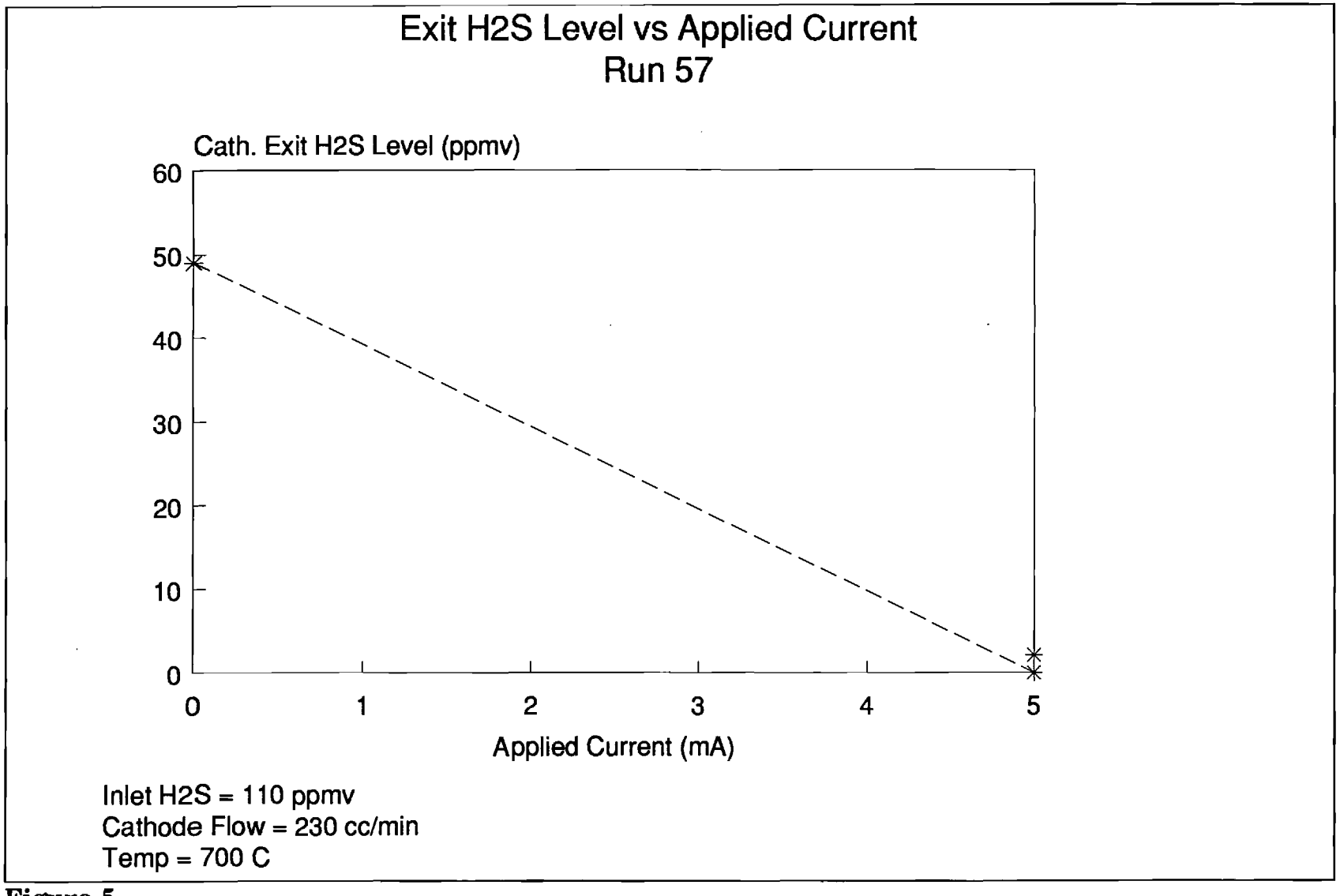

Exit H2S Level vs Applied Current
Run 57
Cath. Exit H2S Level (ppmv)
60
50
40
30
20
10
0
0
1
2
3
4
5
Applied Current (mA)
Inlet H2S = 110 ppmv
Cathode Flow = 230 cc/min
Temp = 700 C

Figure 5

Table IV. Run 57 Data.

Run 57

Cathode = lithiated Ni Anode = lithiated Ni

Membrane = two tapes of MgO layered with two mats of ZYW-30A (zirconia cloth) (wick from ZYW-30A into carbonate reservoir)

Electrolyte = 0.8 mole% sulfide in eutectic Li/K carbonate

Housings = type 316 SS with Al paint coating

Inlet Gas Composition = 110 ppm H_2S
18% CO_2, 45% CO, Balance H_2 (dry comp., before shift reaction)
Hydrated to 3.1% H_2O (before shift reaction)

Cathode Flow = 230 cc/min Anode Flow = 80 cc/min

Run Temp = 700°C

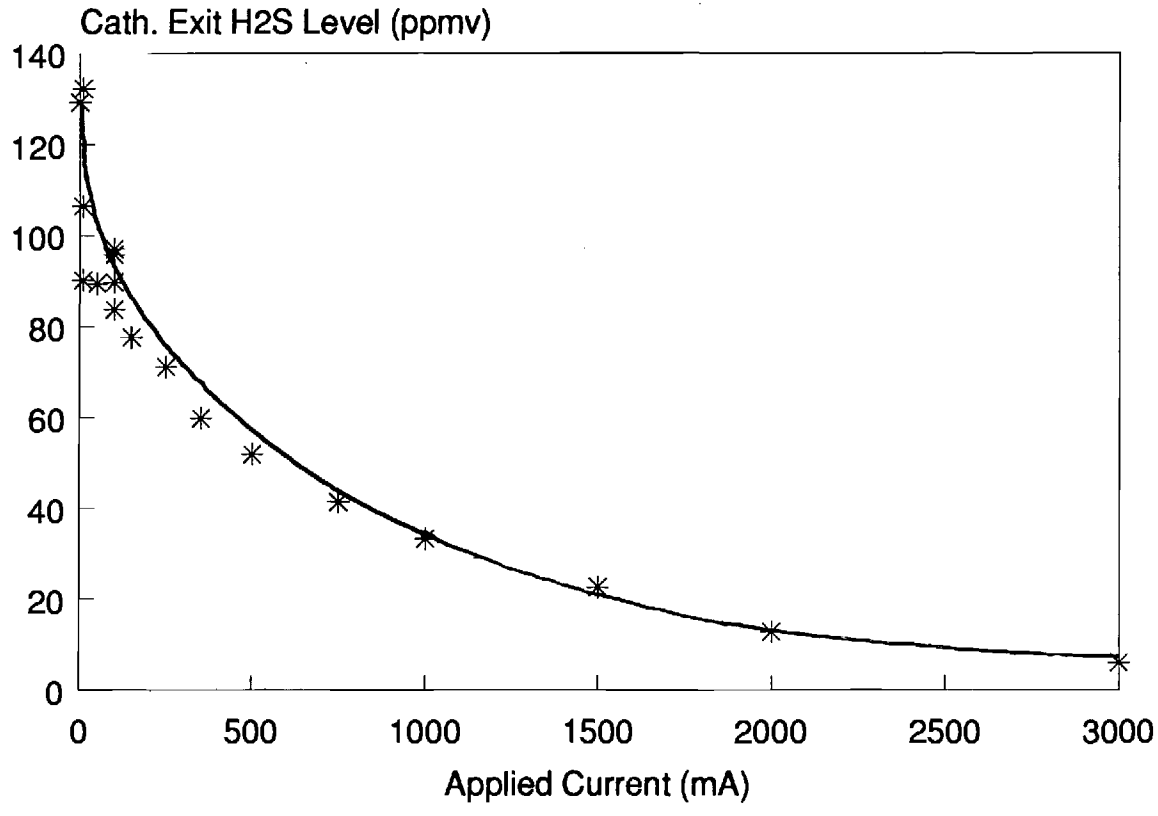
I_{app} (mA)	E_{C-A} (Volts)	Cath. Exit H_2S (ppm)
0	-0.545	49.0
5	-0.275	0.0
5	-0.250	2.1

Run 58

This experimental run also used lithiated Ni electrodes. In this experiment, the membrane was a hot pressed Molten Carbonate Fuel Cell (MCFC) membrane provided by Gas Research Institute (GRI). This structure is a 50/50 weight mixture of $LiAlO_2$ and eutectic Li/K carbonate. The housings were MACOR (with a stainless steel coil in the feed gas line to act as a shift reactor) and aluminum foil gaskets were used. Excess Li_2CO_3 (for reaction with the Al gaskets in conversion to $LiAlO_2$) was sprinkled on the membrane surface with enough Li_2S to bring the electrolyte to 0.8 mole% sulfide.

After the electrolyte was molten, fuel gas with composition 17.3% CO_2, 42.2% CO, 3.3% H_2O, 37.1% H_2, (after shift reaction) and 117 ppmv H_2S was fed to the cell. This gives an equilibrium sulfide level of 0.65 mole%. The calculated gas phase limiting current density at this temperature was found to be 1.31 mA/cm^2 and the membrane limiting current density was estimated to be 1.53 mA/cm^2.

H_2S removal data (see Figure 6 and Table V), anodic CO_2 production data (see Table V), and cross-cell potential data (see Table V) was taken. Examination of Figure 6 shows the most dramatic H_2S reduction takes place at currents less than 10 mA (1.23 mA/cm^2). Beyond this, diffusion of H_2 across the cell decreases H_2S current efficiencies in favor of CO_2 production with applied current. Cross-cell potentials were very high at large applied currents (> 500 mA). This was due to concentration effects as the cathode gas was depleted of H_2O by the carbonate transport reaction. H_2S levels were driven as low as 6 ppmv even with H_2 cross-over.



Inlet H2S = 117 ppmv
Cathode Flow = 200 cc/min
Temp = 700 C

Figure 6

Table V. Run 58 Data.

Run 58

Cathode = lithiated Ni Anode = lithiated Ni

Membrane = GRI MCFC membrane spiked with Li_2S to 0.8 mole% ($LiAlO_2$ matrix)

Electrolyte = 0.8 mole% sulfide in eutectic Li/K carbonate

Housings = MACOR with SS shift reactor

Gaskets = Al foil

Inlet Gas Composition = 104 ppm H_2S
18% CO_2, 45% CO, Balance H_2
(dry comp., before shift reaction)
Hydrated to 3.1% H_2O (before shift reaction)

Cathode Flow = 200 cc/min Anode Flow = 175 cc/min

Run Temp = 700°C

I_{app} (mA)	E_{C-A} (Volts)	Cathode Exit H_2S (ppm)	Anode Exit CO_2 (mole%)
0		129.3	
10		132.5	
10	+0.030	106.5	
100	-0.790	95.8	
100	-0.941	89.7	1.00
100	-0.962	97.0	
10	-0.160	90.2	0.20
50	-0.405	89.4	0.45
100	-0.816	83.7	0.95
150	-1.571	77.6	1.50
250	-2.090	71.1	2.40
350	-2.450	59.7	
500	-2.640	51.9	
750		41.4	7.10
1000	-3.750	33.3	9.00
1500	-5.510	22.6	13.5
2000	-6.160	12.8	
3000	-12.08	6.0	

Run 59

This experimental run used two mats of zirconia cloth that were densified from 83% voids to 72% voids by soaking in an ethyl alcohol slurry of $LiAlO_2$ (slurry 20 wt% $LiAlO_2$). Particles of $LiAlO_2$ where suspended within the ZrO_2 mesh after the water was evaporated away. No tapes of MgO were used in this experiment. The electrodes were both lithiated nickel. The electrolyte was pressed and loaded as a disk into the cell prior to heat-up. The electrolyte composition was 0.8 mole% sulfide and the balance was eutectic carbonate. The housings were MACOR and aluminum foil gaskets were used.

After melting the electrolyte into the matrix, fuel gas of composition 14.4% CO_2, 45.1% CO, 6.2% H_2O, and 34.2% H_2 (after shift reaction) with 85.7 ppm H_2S was started to the cell. This gives an equilibrium sulfide level of 0.48 mole %. The gas phase limiting current density was estimated to be 1.06 mA/cm^2 and the membrane limiting current density was estimated to be 1.5 mA/cm^2.

H_2S removal data (see Figure 7 and Table VI) and cross-cell potential data (see Table VI) were taken. The inlet H_2S level was 85.7 ppm, but with zero current applied to the cell, the exit H_2S level was seen to be 165 ppm. This was due to excess sulfide initially present in the electrolyte. With application of current, H_2S levels were driven as low as 73 ppm with 400 mA applied to the cell (50.5 mA/cm^2). Hydrogen cross over hampered H_2S removal efficiency causing higher current levels to be needed to achieve removal. With higher currents came higher cross-cell potentials until the carbonate transport region was reached. Here, H_2S removal

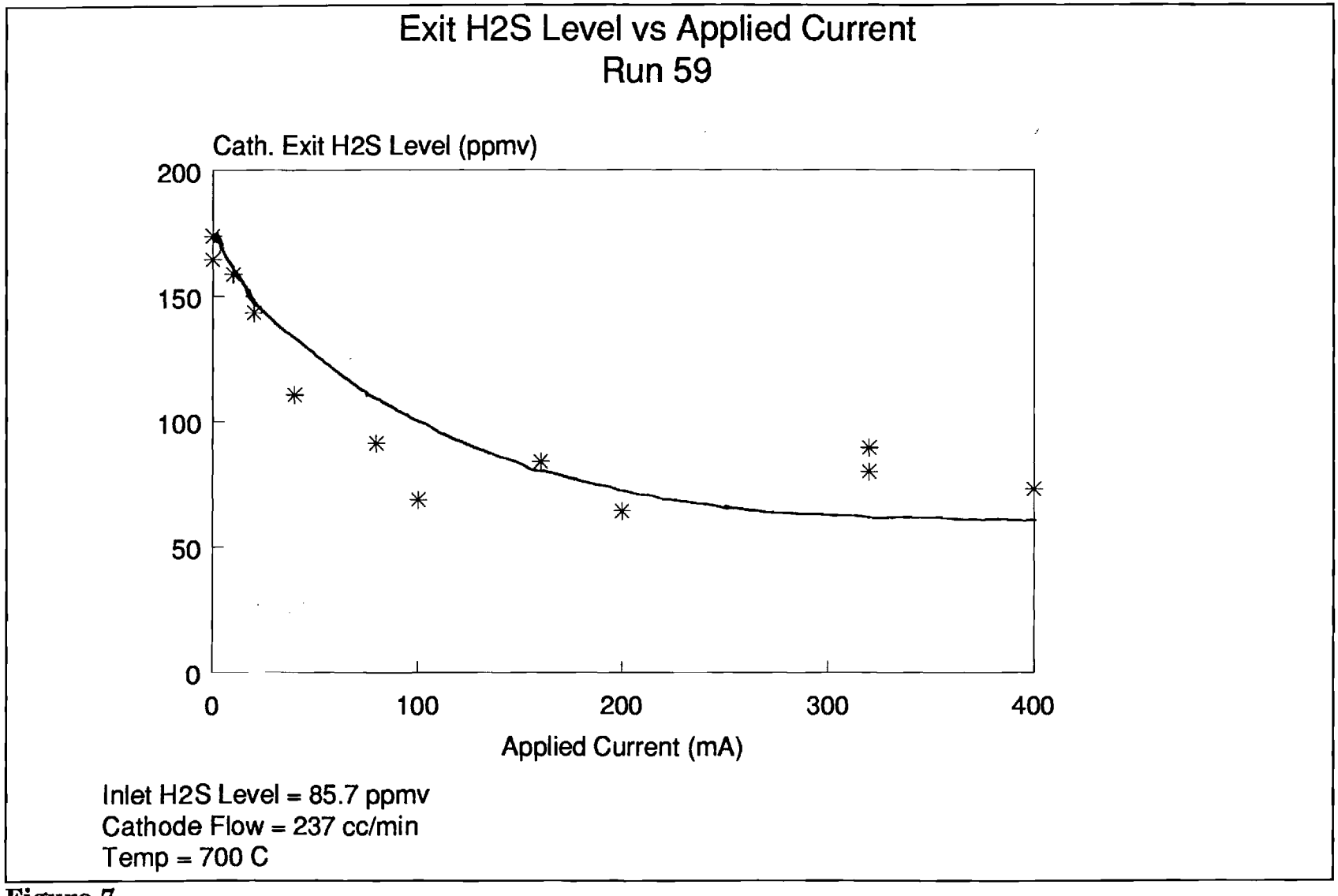

Exit H2S Level vs Applied Current
Run 59
Cath. Exit H2S Level (ppmv)
200
150
100
50
0
0
100
200
300
400
Applied Current (mA)
Inlet H2S Level = 85.7 ppmv
Cathode Flow = 237 cc/min
Temp = 700 C

Figure 7

Table VI. Run 59 Data.

Run 59

Cathode = lithiated Ni Anode = lithiated Ni

Membrane = two mats of ZyW-30A (zirconia cloth) densified with $LiAlO_2$

Electrolyte = 0.8 mole% sulfide in eutectic Li/K carbonate

Housings = MACOR with SS shift reactor

Gaskets = None

Inlet Gas Composition = 85.7 ppm H_2S
18% CO_2, 45% CO, Balance H_2
(dry comp., before shift reaction)
Hydrated to 3.1% H_2O (before shift reaction)

Cathode Flow = 237 cc/min Anode Flow = 100 cc/min

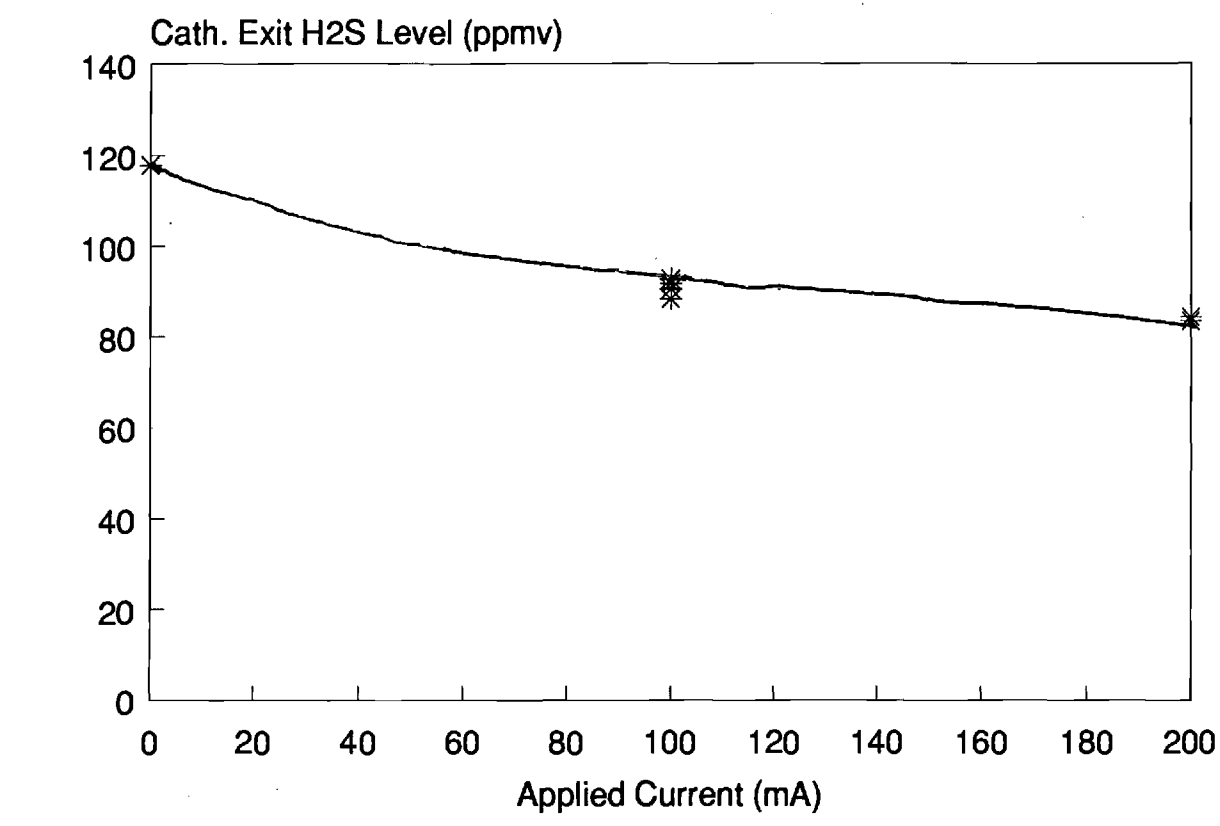
Run Temp = 700°C

I_{app} (mA)	E_{C-A} (Volts)	Cathode Exit H_2S (ppm)	Anode Exit CO_2 (mole%)
0	-0.014	164.6	0.40
10	-0.064	158.7	0.30
20	-0.131	143.4	0.30
40	-0.350	110.6	0.10
80	-0.549	91.4	0.20
160	-0.908	84.1	0.30
320	-1.362	89.7	0.40
320	-1.392	80.1	0.4
0	+0.002	174.0	
100	-0.713	69.0	
200	-1.261	64.4	
400	-2.230	73.2	

stopped due to theconcentration preference for carbonate transport.

Run 62

This experimental run was also identical in set-up to run 60. The zirconia mats were densified to 64 void %. Only enough electrolyte was added to wet the membrane, extra electrolyte was slowly added after the cell had reached run temperature to react with the Al gaskets. Once the electrolyte had melted, fuel gas of composition 14.4% CO_2, 45.1% CO, 6.2% H_2O, 34.2% H_2 (after the shift reaction at 700°C) with 120.4 ppmv H_2S. H_2S removal data was taken at 216 cc/min and a temperature of 700°C. At this temperature and gas composition, the equilibrium sulfide level in the electrolyte is calculated to be 0.68%. The gas phase limiting current density is 1.33 mA/cm^2 and the membrane limiting current density is 2.10 mA/cm^2. A second set of H_2S removal data was taken at a flow of 100 cc/min and a temperature of 750°C (gas composition 13.6% CO_2, 45.8% CO, 6.9% H_2O, 33.4% H_2 with 93.6 ppmv H_2S) (see Figure 8, Figure 9, and Table VII). At this temperature and gas composition, the membrane equilibrium sulfide level was estimated to be 0.91 mole% sulfide. The gas phase limiting current density was estimated to be 1.15 mA/cm^2 and the membrane limiting current density 2.82 mA/cm^2. Anodic CO_2 production was also monitored (see Table VII) and cross-cell potentials were recorded for 100 cc/min and run temperature of 750°C (see Table VII). Comparison of Figure 8 and Figure 9 shows that H_2S removal efficiency is improved by lower flow rates (higher residence time) and higher temperatures (higher limiting current densities).



Inlet H2S Level = 120.4 ppmv
Cathode Flow = 216 cc/min
Anode Flow = 42 cc/min

Figure 8

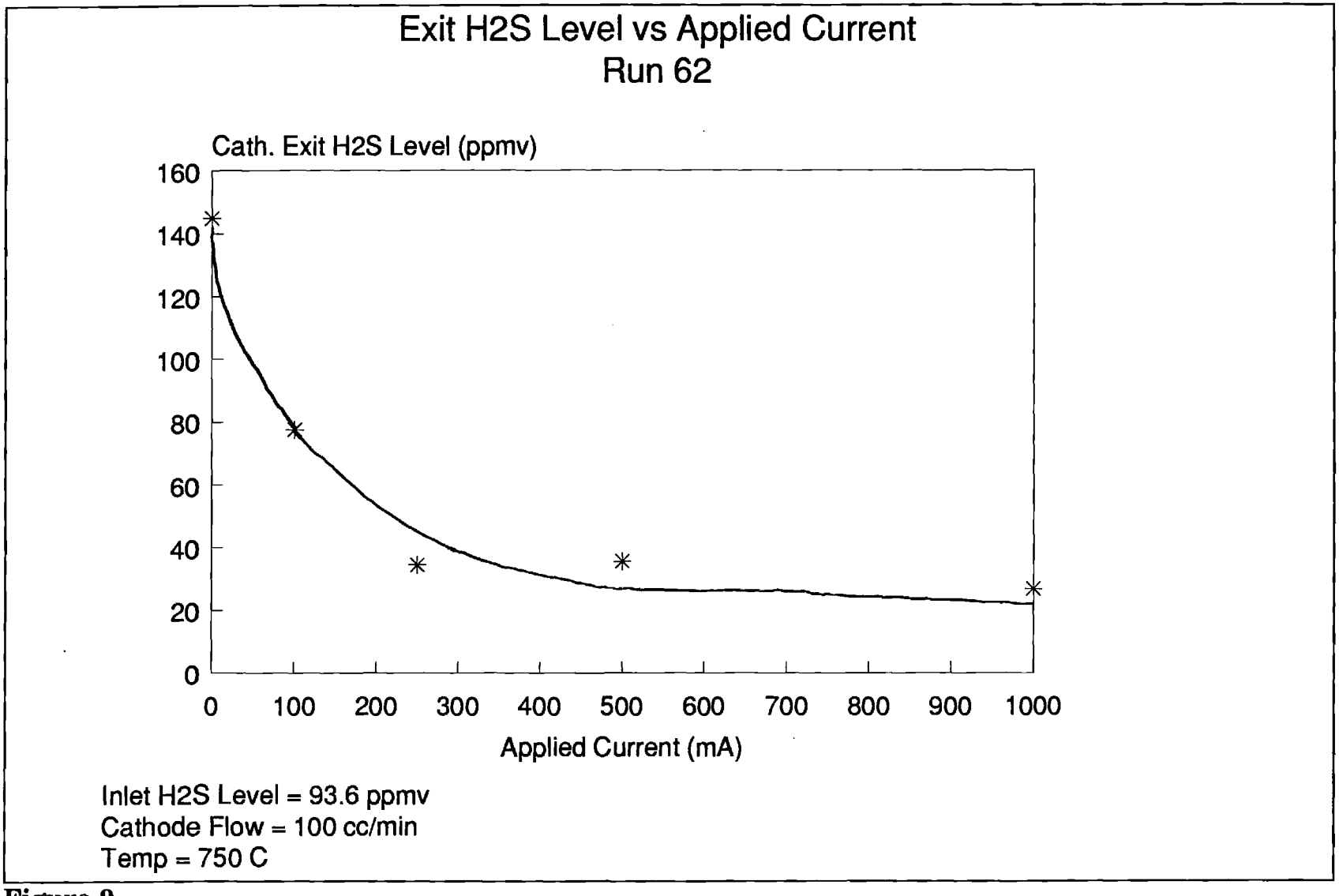

Exit H2S Level vs Applied Current
Run 62
Cath. Exit H2S Level (ppmv)
160
140
120
100
80
60
40
20
0
0
100
200
300
400
500
600
700
800
900
1000
Applied Current (mA)
Inlet H2S Level = 93.6 ppmv
Cathode Flow = 100 cc/min
Temp = 750 C

Figure 9

Table VII. Run 62 Data.

Run 62

Cathode = lithiated Ni Anode = lithiated Ni

Membrane = two mats of ZyW-30A (zirconia cloth) densified with sub-micron zirconia from Zircar Inc.

Electrolyte = 0.8 mole% sulfide in eutectic Li/K carbonate

Housings = MACOR with SS shift reactor

Gaskets = Al foil

Inlet Gas Composition = 120.4 ppm H_2S
18% CO_2, 45% CO, Balance H_2
(dry comp., before shift reaction)
Hydrated to 3.1% H_2O (before shift reaction)

Cathode Flow = 216 cc/min Anode Flow = 42 cc/min

Run Temp = 700°C

I_{app} (mA)	E_{C-A} (Volts)	Cathode Exit H_2S (ppm)	Anode Exit CO_2 (mole%)
0	-0.100	117.8	
100	-1.370	91.8	1.40
100	-1.419	92.8	1.40
100	-1.501	92.7	1.40
200	-2.370	84.3	2.60
200	-2.390	83.4	2.60
100	-1.406	88.4	1.40
100	-1.448	90.6	1.40

Inlet Gas Composition = 114.7 ppm H_2S

Cathode Flow = 100 cc/min Anode Flow = 58 cc/min

Run Temp = 750°C

I_{app} (mA)	E_{C-A} (Volts)	Cathode Exit H_2S (ppm)	Anode Exit CO_2 (mole%)
0	+0.045	144.9	0.33
1000	-4.980	26.8	9.58
500	-3.370	35.6	5.58
250	-2.270	34.5	3.48
100	-1.652	77.6	1.91

Run 65

This experimental run used 1 mat of 30 mil zirconia cloth which was rigidized to 60.8% and two tapes of MgO/ZrO_2 in vinyl binder. The electrolyte was eutectic carbonate and was added to the cell as a pressed disk. The electrodes were lithiated Ni. The housings were MACOR and Al foil gaskets were used. The run temperature was 650°C. After binder burnout and electrolyte melting, fuel gas of composition 15.2% CO_2, 44.2% CO, 5.4% H_2O, 35.0% H_2 with 18.8 ppmv H_2S was put through the cell. This gas composition and temperature gives an equilibrium membrane sulfide level of 0.06 mole% sulfide. The gas phase limiting current density is estimated to be 0.18 mA/cm^2 and the membrane limiting current density is 0.34 mA/cm^2.

H_2S removal data was taken at cathodic flow rates of 200 cc/min and 100 cc/min (see Figure 10, Figure 11, and Table VIII). Cell polarization data was also take at these flow rates (see Table VIII). Anodic CO_2 production data was also taken at cathodic flow of 100 cc/min (see Table VIII).

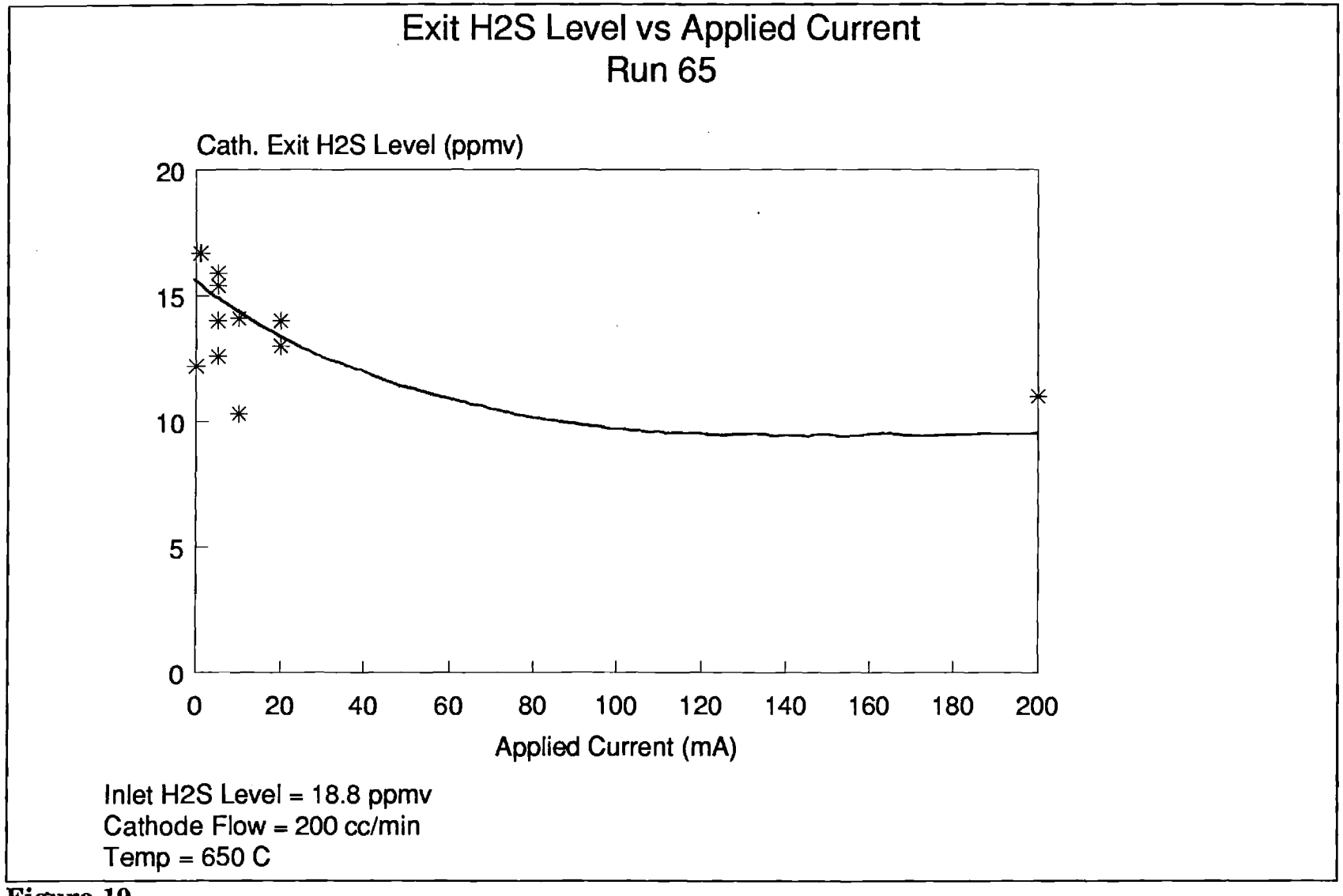

Exit H2S Level vs Applied Current
Run 65
Cath. Exit H2S Level (ppmv)
20
15
10
5
0
0
20
40
60
80
100
120
140
160
180
200
Applied Current (mA)
Inlet H2S Level = 18.8 ppmv
Cathode Flow = 200 cc/min
Temp = 650 C

Figure 10

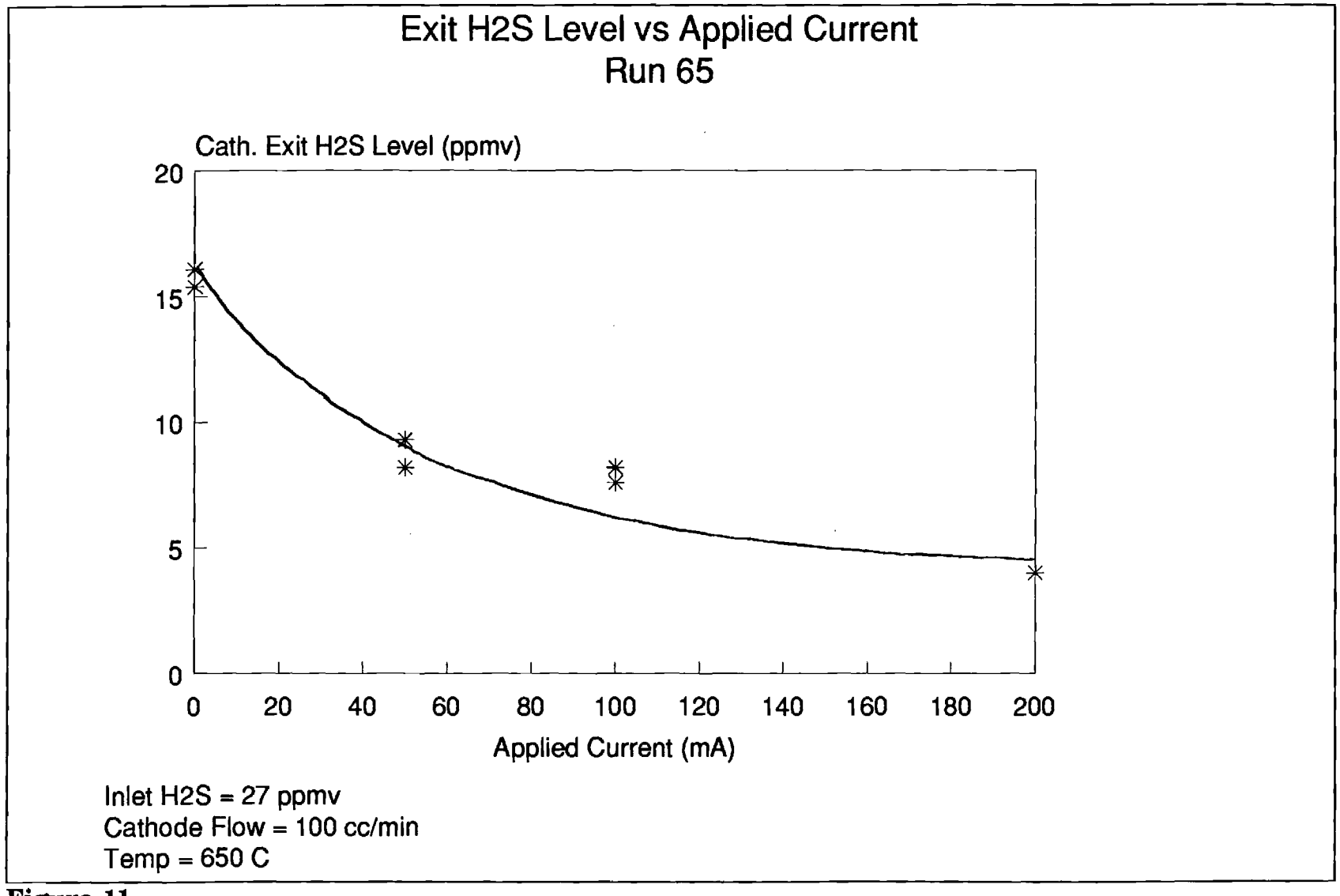

Exit H2S Level vs Applied Current
Run 65
Cath. Exit H2S Level (ppmv)
20
15
10
5
0
0
20
40
60
80
100
120
140
160
180
200
Applied Current (mA)
Inlet H2S = 27 ppmv
Cathode Flow = 100 cc/min
Temp = 650 C

Figure 11

Table VIII. Run 65 Data.

Run 65

Cathode = lithiated Ni Anode = lithiated Ni

Membrane = one mat of ZyW-30A (zirconia cloth) densified with sub-micron zirconia from Zircar Inc. layered with two tape casts of ZrO_2/MgO

Electrolyte = eutectic Li/K carbonate

Housings = MACOR with SS shift reactor

Gaskets = Al foil

Inlet Gas Composition = 19 ppm H_2S
18% CO_2, 45% CO, Balance H_2
(dry comp., before shift reaction)
Hydrated to 3.1% H_2O (before shift reaction)

Cathode Flow = 200 cc/min Anode Flow = 100 cc/min

Run Temp = 650°C

I_{app} (mA)	E_{C-A} (Volts)	Cathode Exit H_2S (ppm)
1.0	-0.163	16.7
5.0	-0.208	15.9
5.0	-0.209	12.6
5.0	-0.207	15.4
5.0	-0.241	14.0
10	-0.242	10.3
10	-0.241	14.1
20	-0.319	14.0
20	-0.319	13.0
200	-0.780	11.0
0	-0.171	12.2

Inlet Gas Composition = 27 ppm H_2S

Cathode Flow = 100 cc/min Anode Flow = 100 cc/min

I_{app} (mA)	E_{C-A} (Volts)	Cathode Exit H_2S (ppm)	Anode Exit CO_2 (mole%)
0	-0.123	15.4	
0	-0.069	16.1	0.80
0	-0.116		0.50
200	-0.778		4.17
200	-0.800		4.34
200		4.0	4.62
100	-1.015	7.6	2.08
100	-1.500	8.2	2.97
50	-1.245	9.3	
50	-1.381	8.2	

Unsuccessful Runs

Run 60

This experimental run used two zirconia mats that were densified with sub-micron particles of ZrO_2 in aqueous solution purchased from Zircar, Inc. This rigidizer is composed of 44 wt% ZrO_2, 8 wt% Acetic acid, 3 wt% Y_2O_3, in an aqueous slurry. Mats were densified by soaking in rigidizing solution under a vacuum to pull air out of the woven cloth and facilitate complete wetting. These were then dried and soaked again. This process was repeated for three consecutive soakings. These mats were densified to 66 void%. The electrolyte was 0.8% sulfide and was pressed into a disk and loaded into the cell to be melted in-situ. The electrodes were lithiated nickel and the housings were MACOR with aluminum foil gaskets.

Poor electrical contacts between the electrodes and the membrane lead to high cell resistance and high cross-cell potentials. The cell was shut down before any useful data was taken.

Run 61

This experimental run was identical in set up to run 60. Excess electrolyte was also added to accommodate reaction of Li_2CO_3 with the Al foil to form $LiAlO_2$. The rate of this reaction is evidently slow, however, since the excess electrolyte flooded the anode channels and froze in the exit anode tube. This caused a pressure spike on the anode side of the cell which ruptured the membrane. The cell was shut

down before any useful data was taken.

Run 63

This experimental run used Si_3N_4 tapes with vinyl binder as the membrane support material. Eutectic carbonate electrolyte was also added to the membrane by mixing in a 50/50 weight mixture with the same binder material and laminating the structure together under pressure. The electrodes in this experiment were both lithiated Ni and the housing was MACOR. No aluminum foil gaskets were used.

The cell was heated under O_2 to 520°C. Cross-flow between the cathode and the anode side of the cell indicated that the membrane had lost integrity. No amount of electrolyte added corrected the situation. The cell was shut down before any useful data could be taken.

Run 64

This experimental used lithiated Ni as both the cathode and the anode. The membrane was a single mat of 15 mil thick zirconia cloth which was rigidized to 66 void%. This was layered with two tapes of MgO within the vinyl binder. The housings were MACOR and no gaskets were used. The electrolyte was soaked into the electrodes previous to run start-up. Since the electrodes could not hold all of the required electrolyte, the remainder was sprinkled onto the membrane before assembly.

The cell was heated under O_2 to 300°C over a 3 hour period and then switched to N_2 for the final heating to 600°C. No seals were formed on either side of the cell.

Cross-flow between the cathode and the anode could not be controlled. When the cell was shut down, it was seen that carbon build-ups had formed the cell housings apart and damaged the membrane. This was from pyrolyzed binder material from incomplete burn-out. No useful data was taken.

Summary

Polishing application (100 ppmv H_2S to less than 5 ppmv H_2S) of this technology to coal gasification synthesis gas has been repeated with both MACOR and 316 Stainless Steel housings. Polishing application has further been demonstrated at removing H_2S to below 5 ppmv with only 16 ppm entering the cell.

Planned Work for Next Quarter

Work will continue with the stainless steel housings. Priority will be placed on improving H_2S removal efficiency by developing even more H_2 impermeable membranes.

DOE F 1332.16 (10-84)
(Formerly RA-427)

OMB Approval
No. 1910-1400

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Jack Winnick, Professor

Organization
Georgia Tech Research Corporation

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Signature [illegible] | **Phone** (404) 894-2839 | **Date** 11/12/1992

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Quarterly Progress Report:

High Temperature Electrochemical Separation Of H2S from Coal Gasification Process Streams

Grant DE-PS22-91PC91282

July 1, 1992 - September 30, 1992

by

Professor Jack Winnick

Georgia Institute of Technology

School of Chemical Engineering

Atlanta, GA 30332-0100

Objective

A method of polishing coal synthesis by an electrochemical operation is being perfected. The operation which takes advantage of an electrochemical potential gradient rather than conventional techniques, removes the poisonous H_2S from the coal gas stream leaving only H_2 to enrich the exiting polished gases. Sulfur is the by-product which is swept away by an inert sweep gas and later condensed. The technology is attractive due to aesthetics as well as economics when compared to other alternatives.

Current experiments are based on improving selective removal from low initial H_2S concentrations (10 ppm). High flow rate data is also being investigated along with developing a consistent method of sealing the cell housings. The latest option for consistent removal and seals is the Zircar manufactured membranes, which have shown promise prompting further testing.

Introduction

A schematic of the technology being used is presented in Figure 1. The process gas, cleansed of particulates, is passed by the cathode. Here the best Lewis acid(electron acceptor), will be reduced. In this case H_2S is favored, resulting in the following:

$$H_2S + 2e^- \rightarrow S^{2-} + H_2$$

The sulfide ions are transported, by current through the membrane. Once the sulfide ion reaches the anode side, oxidization to elemental sulfur occurs.

$$S^{2-} \rightarrow 1/2S_2 + 2e^-$$

The sulfur vapor is then carried away by an inert gas, preferable N_2 due to low cost. The vaporous sulfur is condensed downstream.

Experimental Results

Five experimental runs using simulated coal gas were attempted this quarter. Runs 1-5 varied in the membranes used as well as the technique to seal the housings. Runs 4 & 5 were successful in removing H_2S with applied current. Run 1 was successful in maintaining seals but not in removal. Runs 2 & 3 were not successful. A summary of these experiments follows.

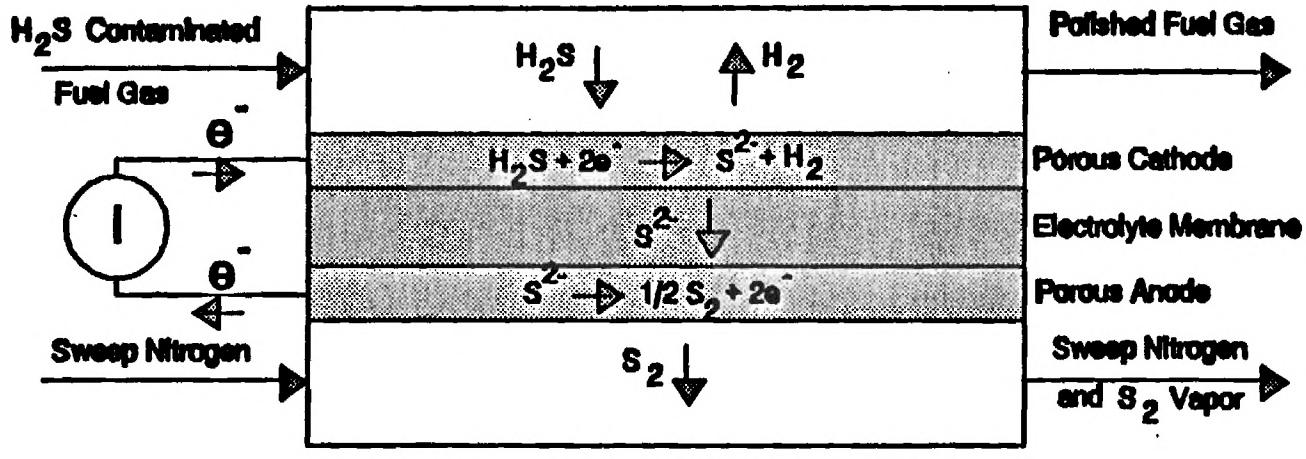

Figure 1. Schematic of H_2S Removal Cell.

Successful Runs

Run #4

This experimental run used a combination of two thin Zirconia weave mats. These mats were hardened using the zirconia rigidizer supplied by Zircar. The mats were then combined and air dried on a strip of Teflon to prevent surface bonding. The mats were covered with weight paper and an iron mesh atop to prevent warping of the membrane. After drying, the membrane was baked in a high temperature oven to burn off the weight paper. The membrane was then autoclaved to insure uniformity. The porosity of the membrane was estimated at 68%. Both cathode and anode electrodes were lithiated Ni, which was converted in-situ to a mixture of NiO and Ni on the cathode side. The anode was converted completely to NiO due to the oxidizing nature of the anode. Li/K eutectic carbonate electrolyte was prepressed and inserted between the cathode housing and the rigidized Zirconia membrane. The housings were made of MACOR, which is a machineable ceramic. The inlet synthesis gases were allowed to go to their equilibrium concentrations (6.0% CO_2, 25.9% CO, 6.4% H_2O, 61.6% H_2, and 14 ppm H_2S) via a stainless steel water-gas shift reactor, before entering the cathode housing. The electrolyte was allowed to go its equilibrium sulfide concentration (0.1 mole%). Aluminum foil gaskets, coupled with an electrolyte-water solution, were used on both housings for a sealant.

The temperature and flow rate were maintained at 650^{0}C and 215 cc/min respectively. Inlet concentration was held between 6 and 20 ppm H_2S. As much as 94%

removal with applied current was seen in this experiment as shown in figure 2. The results of both run 4 & 5 are tabulated in table 1. The experiment was shut down due to hydrogen cross-over. Run #4 lasted 163 hours.

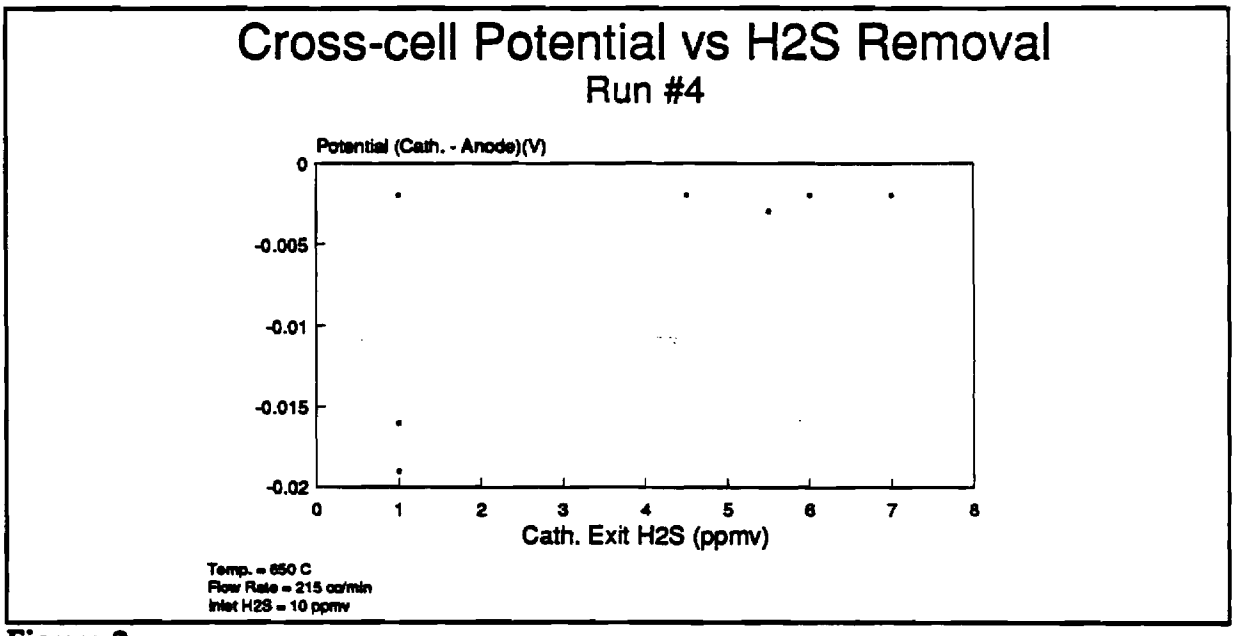

Figure 2

<u>Run #5</u>

This experiment used the Zircar manufactured membranes. The advantages of this membrane are uniform porosity and no warping. Wicking electrolyte into the cell, via the Zircar membrane, rather than using an electrolyte well atop the cathode housing aids in stabilizing the membrane. The Li/K electrolyte was prepressed and placed

between the cathode housing and the manufactured membrane, in the amount corresponding to a 66% membrane porosity. Aluminum foil gaskets, were used on both housings to aid the sealing process. Lithiated Ni electrodes were used allowing them to convert to NiO in-situ. The inlet gas where allowed to reach equilibrium (5.8% CO_2, 25.6% CO, 6.7% H_2O, 65.3% H_2) after the water-gas shift reaction. The equilibrium sulfide concentration in the electrolyte (0.11 mole%) was reached in-situ.

Temperature in this experiment was maintained at 650°C, flow rate was varied from 170 to 814 cc/min. The results are shown in table 1 along with these from run #4. Removal at all flow rates exceeded 90% with applied current as shown in figure 3. The cell was shut down due to an increasing membrane thickness (δ). This was caused by excess addition of electrolyte, resulting in increased resistance to diffusional transport of sulfide:

$$i_d = n F \rho (x_{cath} - x_{an}) / \delta$$

$$IR = n F \ln (i / i_d)$$

Table I. Experimental Results for Runs #4 & #5

Temp. (°C)	Flow-Rate (cc/min)	Residence Time (sec.)	Inlet H_2S (ppm)	Exit H_2S (@ I_{app})	I_{app} (mA)	E_{c-a} (Volts)
650	170	0.197	25	1	1	-0.190
	225	0.146	8.5	1	2	-0.013
	375	0.089	22	1	2	-0.003
	580	0.058	20	1	5	-0.047
	814	0.041	22	1	5	-0.199

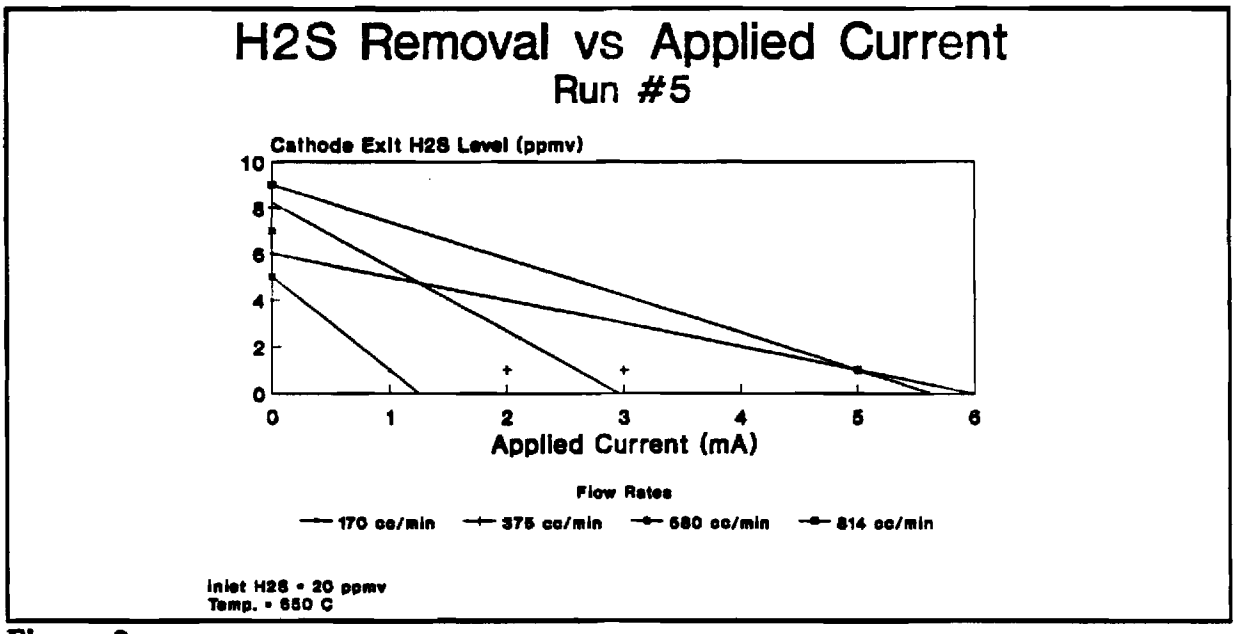

Figure 3

as δ increases, diffusional current decreases; therefore, the resistance to ionic transport increases, reducing sulfide migration across the cell. The cell was shut down after 208 hrs.

Unsuccessful Performance

Run #1

This experiment utilized stainless steel housings, the purpose of which is longevity. The housings were initially painted with aluminum paint (29 wt% Al), once the paint dried, the housings were placed in an oven and baked at 500°C for 3 hrs. This converted the Al to alumina which can aid in sealing by reacting with the Li in the Li/K eutectic carbonate electrolyte to form $LiAlO_2$. A manufactured Zircar membrane was

used along with a pressed disk of the aforementioned electrolyte. The electrodes were lithiated Ni and allowed to convert to NiO in-situ. The success of this experiment came from the development of strong seals that withheld back pressures as high as 30 mm H_2O. No effective removal data was taken during this run , but the experiment lasted for 453 hours, which is the longest to date.

Run #2 - #3

These experiments are combined due to the usage of the same type Zircar manufactured membrane for both. Lithiated Ni were used as electrodes and aluminum paint was applied to the MACOR housings for sealant. The electrolyte, sized to fill the 66% voids in the membrane, was prepressed and placed between the cathode and Zircar membrane.

Run #2 lasted only 48 hrs due to carbon build up between the cathode electrode and the membrane. This was caused by the Bourdouart reaction, avoidable by increasing hydration of the fuel gas:

$$H_2O + CO \rightarrow H_2 + CO_2$$

$$2CO \rightarrow C + CO_2$$

Run #3 lasted only 24 hrs due to cracks in the membrane, causing diffusion of hydrogen, and lack of seals. There was no outflow of gas on either side of the cell.

Summary

The manufactured Zircar membranes have shown promise obtaining removals of over 90% with applied current. The rigidized mat produced in our laboratory produced excellent removal. The most exciting aspect of the quarter was the removal at high flow rates. Although seals were a problem, run #1 showed promise in that aspect.

Work for Next Quarter

Work for next quarter will deal with improving seals by using the method suggested in run #1. Also the rigidized mats produced in our lab will be further investigated due to the economic advantage over the manufactured membranes. Once the cell is running removal seems almost assured.

References

1. Weaver, D., Electrochemical Removal of Hydrogen Sulfide From Multi-Component Gas Streams, PhD Thesis, Georgia Institute of Technology, 1988.

2. Alexander, S., Electrochemical Removal of H_2S from Fuel Gas Streams, PhD Thesis, Georgia Institute of Technology, 1992.

Quarterly Progress Report:

High Temperature Electrochemical Separation Of H2S from Coal Gasification Process Streams

Grant DE-PS22-91PC91282

October 1, 1992 - December 30, 1992

by

Professor Jack Winnick

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School of Chemical Engineering

Atlanta, GA 30332-0100

Objective

A method of polishing coal synthesis by an electrochemical operation is being perfected. The operation which takes advantage of an electrochemical potential gradient rather than conventional techniques, removes H_2S from the coal gas stream leaving only H_2 to enrich the exiting polished gases. Sulfur is the by-product which is swept away by an inert sweep gas and condensed downstream. The technology is attractive due to aesthetics as well as economics when compared to other alternatives.

Current experiments are based on improving selective removal from low initial H_2S concentrations (10 ppm) and developing a consistent method of sealing the cell housings. The best option uses the Zircar manufactured membranes, or a lab replication of the Zircar manufactured membranes. Both result in similar removals, over 80% with applied current.

Another membrane, an electrolyte filled rigid tile, was examined this quarter. Elimination of prepressing and addition of the electrolyte into the cell housing relieves calculation errors, dealing with electrolyte content, needed to fill the voids of the membrane and to react with the alumina for seal formation.

Introduction

A schematic of the technology being used is presented in Figure 1. The process gas, cleansed of particulates, is passed by the cathode. Here the best Lewis acid (electron acceptor), will be reduced. In this case H_2S is favored, resulting in the following:

$$H_2S + 2e^- \rightarrow S^{2-} + H_2$$

The sulfide ions are transported, by current through the membrane. Once the sulfide ion reaches the anode side, oxidization to elemental sulfur occurs.

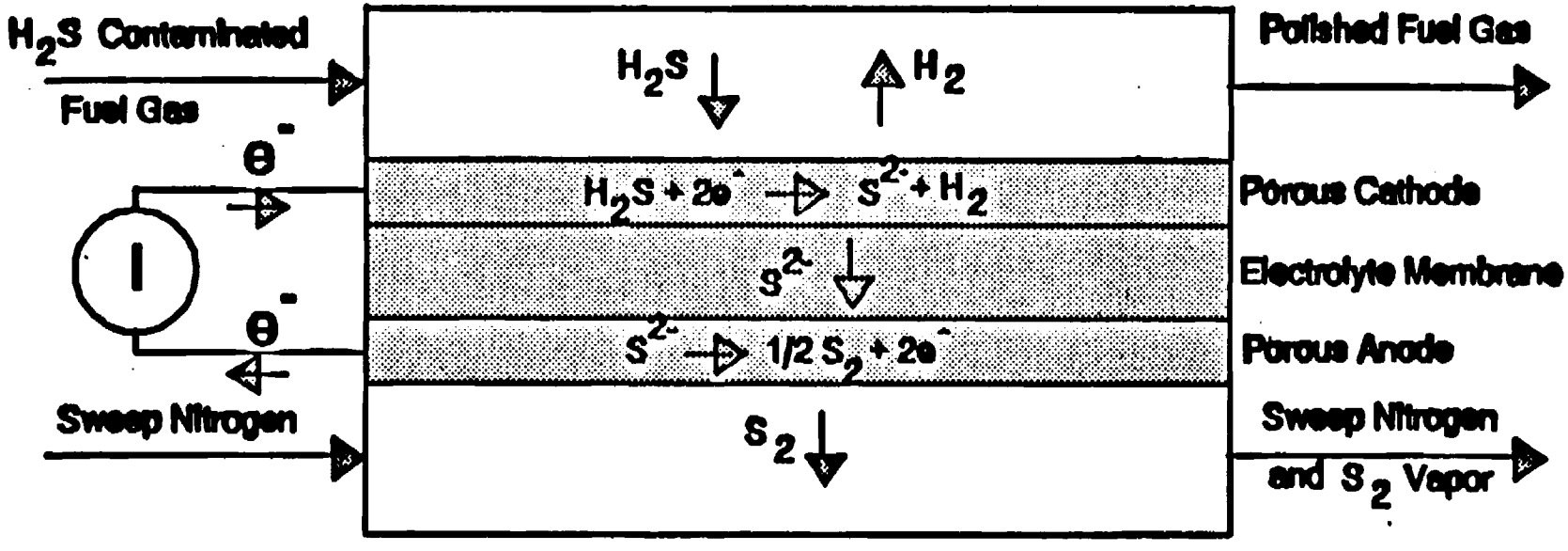
$$S^{2-} \rightarrow 1/2S_2 + 2e^-$$

The sulfur vapor is then carried away by an inert gas, preferable N_2 due to low cost. The vaporous sulfur is condensed downstream.

Experimental Results

Experimental results presented are based on five experiments with initial H_2S concentrations of ~100 ppm. In order to represent probable industrial conditions, variables such as flow rates, selectivity of the membranes, and cell housing seals, were of primary concern in these experiments. Over 90% Removal of H_2S with applied current has been recorded with similar conditions.

Cell housing materials used for runs 6 - 9 were made of machineable ceramic (MACOR), while stainless steel housings were used in run 10. Cathode and anode electrodes consisted of Ni which oxidized in-situ to form NiO. All runs were unsuccessful in removing H_2S due predominantly to H_2 cross-over, caused by cracking


H_2S Contaminated
Fuel Gas
e^-
I
e^-
Sweep Nitrogen
H_2S
H_2
$H_2S + 2e^- \rightarrow S^{2-} + H_2$
S^{2-}
$S^{2-} \rightarrow 1/2\ S_2 + 2e^-$
S_2
Polished Fuel Gas
Porous Cathode
Electrolyte Membrane
Porous Anode
Sweep Nitrogen
and S_2 Vapor

of the membranes. A summary of these experiments is presented in following paragraphs.

Run #6

This experimental run used a rigidized, electrolyte filled membrane, which becomes molten around 550° C. Flow tubes into the cell housings were changed from conventional high temperature, high density ceramic to Silicon Nitride tubing. The purpose being to find a more convenient material to repair if a flow tube was broken. This created leakage problems due to lack of bonding between the tubes and bonding material (adhesive cement). Reversion back to the original ceramic tubing should cure the problem. Aluminum foil gaskets, coupled with an electrolyte-water solution, were used on both housings for a sealant. Initial seals never developed creating deficiencies in fuel gas residence time and interaction at the electrode-electrolyte interface.

The membrane was advantageous in the initial stages because of its pre-electrolyzed make-up, eliminating conventional steps of pre-pressing and infiltration of the electrolyte. However, the tile performed inadequately in the experimental environment. Once molten, the stability of the tile seemed to weaken. The tile transformed into a limp paste, lacking the qualities necessary for electrolyte support or protection from gas cross-over. The cell was shut-down after 166 hours, mainly because of H_2 cross-over due to cracks in the tile.

Run #7

Use of another rigid electrolyte tile failed to provide adequate selectivity from H_2 cross-over. Thermal stress caused by thermocouple damage, lead to severe cracks in the membrane. The thermal stress developed once the thermocouple malfunctioned, causing the temperature in the oven to reach 900° C. When repairing the thermocouple, the temperature plummeted to 400° C. At 400° C the electrolyte solidifies, causing cracks due to expansion. Shut-down occurred 15 hours after start-up.

Run #8

Another run using an electrolyte filled tile failed. Aluminum paint, cooked onto the cell housings, was to provide gas seals. The seals never developed and cross-over progressively worsened with time. Once again the stability of the tile was evidenced due to continual cross-over. The run was shut-down after 24 hours.

Run #9

A laboratory replication of the Zirconia membrane was utilized in this experiment. A combination of two thin weaved Zirconia mats were hardened using the rigidizer supplied by Zircar. The mats were combined and air dried on a strip of Teflon to prevent surface bonding. An iron mesh atop weighing paper covered the mats to prevent warping. After drying, the membrane was baked in a high temperature oven to burn off the weighing paper, then autoclaved to insure uniformity. The porosity was estimated at 80% which indicates not enough rigidizer absorbed in the initial step of

rigidization. In the past, similar experiments were successful with membrane porosities around 65%. Similar porosities must be meet in the future before the run is started. 80% porous membranes do not provide enough stability to protect against gas cross-over. Therefore, cross-over resulted in cell shut-down after 24 hrs.

Run #10

A Zircar manufactured membrane provided the electrolyte support in this experiment. Seals developed by reaction of cooked aluminum paint with lithium in the molten electrolyte. The initial problem was not effected by lack of seals or cross-over, but by carbon formation caused by insufficient H_2O concentration in the water-gas shift reactor. The build-up of carbon formed a barrier to entering gases, leaving the cell inactive. Cell repair, while keeping the electrolyte molten, initially saved the experiment. Once seals redeveloped with no evident cross-over, H_2S (140 ppm) was sent to the cell. Sulfide equilibrium never occurred due to a consistent lack of electrolyte. Continuous addition of electrolyte should have caused flooding of the electrodes but reaction with the aluminum paint exceeded the small estimates of required electrolyte. Future experiments must contend with reactions dealing with seal formation. Also the water-gas shift reaction must be strictly adhered to, due to the consequences of carbon build-up. Shut-down occurred after 140 hours.

Summary

Experimentation with a rigidized, electrolyte filled tile, left much to be desired. The instability of the tiles at molten conditions (> 550° C), provided the necessary mechanism for H_2 to penetrate the membrane. Once H_2 cross-over occurs the entire objective of electrochemical separation becomes nullified. The Zircar membranes used last quarter provided excellent protection against H_2, prompting a reversion back to them. If porosities are strictly adhered to and the water-gas shift is properly handled, the membranes should provide an adequate mechanism for selective H_2S removal.

Work for Next Quarter

Work for next quarter will deal with improving seals on the MACOR housings. Also the rigidized mats produced in our lab will be emphasized due to the economic advantage over the manufactured membranes or electrolyte filled tiles. If a porosity of approximately 66% is achieved, removal seems almost assured, with proper seals.

References

1. Weaver, D., Electrochemical Removal of Hydrogen Sulfide From Multi-Component Gas Streams, PhD Thesis, Georgia Institute of Technology, 1988.

2. Alexander, S., Electrochemical Removal of H_2S from Fuel Gas Streams, PhD Thesis, Georgia Institute of Technology, 1992.

DOE F 1332.16 (10-84)
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No. 1910-1400

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   Jack Winnick, Professor

   Organization
   Georgia Tech Research Corporation

   Signature X | Phone (404) 894-2839 | Date 6-9-93

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   - [ ] b. Report has been sent to responsible DOE patent group for clearance.

Quarterly Progress Report:

High Temperature Electrochemical Separation Of H2S from Coal Gasification Process Streams

Grant DE-PS22-91PC91282

January 1, 1993 - March 30, 1993

by

Professor Jack Winnick

Georgia Institute of Technology

School of Chemical Engineering

Atlanta, GA 30332-0100

Objective

A method of polishing coal synthesis gas by an electrochemical operation is being perfected. The operation which takes advantage of an electrochemical potential gradient rather than conventional techniques, removes poisonous H_2S from the coal gas stream leaving only H_2 to enrich the exiting flue gases. Sulfur is the by-product which is carried away by an inert sweep gas and condensed downstream. The technology is attractive due to aesthetics as well as economics when compared to other alternatives.

Current experiments are focusing on production of selective membranes made of zirconia and improving cell housing seals using Aluminum foil gaskets.

Introduction

A schematic of the mechanism used for electrochemical separation is presented in Figure 1. The process gas, cleansed of particulates, passes over the cathode. Here the best Lewis acid(electron acceptor), will be reduced. In this case H_2S is favored, resulting in the following:

$$H_2S + 2e^- \rightarrow S^{2-} + H_2$$

The sulfide ions are transported, by current through the membrane. Once the sulfide ion reaches the anode side, oxidation to elemental sulfur occurs by the following:

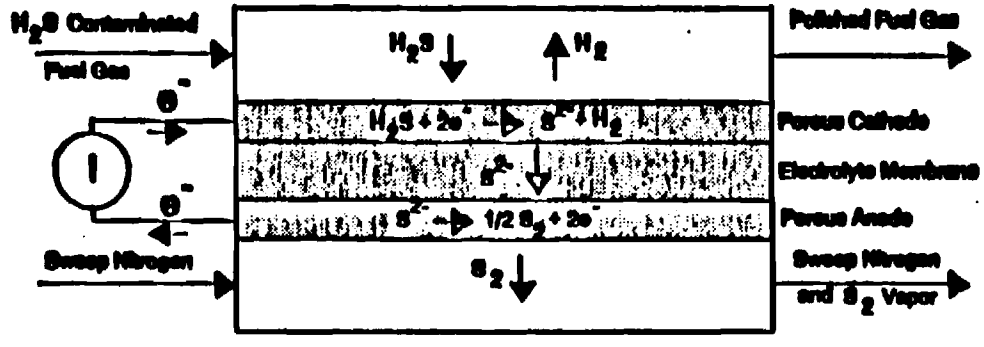
$$S^{2-} \rightarrow 1/2\ S_2 + 2e^-$$

The vaporous sulfur is condensed downstream.

Experimental Results

Four experiments were performed this quarter. The main focus of these experiments dealt with incorporating the rigidized zirconia membranes produced in our laboratory. A detailed description is given in subsequent paragraphs. Other priorities involved material issues relevant to the longevity of the cell housings, cathode stability, and process friendly sealants.

Figure 1 Electrochemical Fuel Gas Desulfurization Cell



Self-produced Membranes

The driving force behind self-preparing membranes is predominantly financial. Conventional rigidized membranes similar to self-developed membranes cost approximately $150.00 per tile (3" x 3" x 0.025"), compared to $10.00 per tile (3" x 3" x .036") for self-produced membranes. The major problem with using the laboratory fabricated membranes arises in the consistency of production. An essential porosity of around 65% must be obtained, according to past experiments, in order to operate the cell efficiently. In the cell environ, the 65% porous membrane, with electrolyte infiltrated, prevents cross-over of harmful amounts of hydrogen and allows a low resistance path for ion diffusion and migration. In order to reach such porosities by laboratory fabrication, the method of rigidization must be performed several times, each reducing the porosity by 10%. Every cycle of rigidization requires drying; thus, putting several mechanical strains on the membrane. All the self-produced membranes that met the 65% porosity perform adequately, but contained micro-cracks from the mechanical strain of rigidization. These micro-cracks allow small amounts of hydrogen to cross the membrane, reducing current efficiency by creating alternate reactions at the anode. The proposed solution to hydrogen cross-over involves application of back pressure from the cathode side of the membrane,

strategically similar to the operation of Molten Carbonate Fuel Cells.

Membrane Preparation

The membrane consist of two thin-weaved zirconia mats (3" x 3" x 0.030"). The initial porosity of the mats falls within the 85% range. The objective is to fill (rigidize) the weave to a porosity of approximately 65%. The material used to rigidize the membrane is an aqueous suspension of sub-micron zirconia particles. The aforementioned mats are submerged in a container full of rigidizer, then placed under a vacuum to evacuate the pores. Once the pores are relieved of gaseous fillers, the rigidizer infiltrates the pores. After infiltration, the membrane is placed on a flat Teflon surface, covered with weighing paper, and constrained from curling by a metal mesh. Once dry the membrane is analyzed for void fraction and re-rigidized if found unacceptable.

Run #11

Stainless steel housed the experiment that focused mainly on removal efficiency. The stainless steel were initially preheated to 600 ^{o}C with a coating of 29 wt% aluminum paint. The Al paint was converted to alumina ex-situ which on contact with lithium carbonate in the electrolyte in-situ forms lithium aluminate at high temperatures. Ni electrodes converted in-situ to NiO

provided sites for the electronation of H_2S. The membrane used was a conventional rigid zirconia membrane, 65% porous, purchased from Zircar.

Carbonate transport, which is the initial test of cell efficiency never reached stoichiometry due to reaction of aluminum paint with the electrolyte. The previous reaction formed strong seals but severely deteriorated ability for efficient removal. Other problems such as clogged flow tubes and loss of electrical contact ultimately terminated the experiment. The cell was operable for 60 hours.

Run #12

Housing materials for this experiment consisted of machineable ceramic(MACOR). Aluminum paint coated the surface and upon heating to 600 ^{o}C, did not convert to alumina as expected. This was evident due to the conductive nature of the coating. Nickel electrodes converted in-situ to nickel oxide provided reaction sites. A Zircar manufactured membrane accommodated the electrolyte made of 62 mole% lithium carbonate and 38 mole% potassium carbonate.

Stoichiometric removal of CO_2 at the cathode provided evidence of adequate cell performance, which incited the addition of H_2S. Equilibrium species concentrations comprised (8.51% CO_2, 23.49% CO, 9.49% H_2O, 58.51% H_2, and 115 ppm H_2S). Stoichiometric current, for a flow of 220 cc/min, required 4 mA. Application of stoichiometric current failed to remove any H_2S. Administering several different

current steps (Table 1) showed that removal was possible but at higher currents.

Table 1. Run #12

I_{app} (mA)	H_2S (ppmv)
700	4
350	8
200	32
100	45
50	140
500	5

The logical explanation arises from certain amounts of current being utilized for side reactions within the electrochemical system. The chemistry involving the aluminum sealant seems to be the most obvious deterrent. Due to past troubles emanating from the same problem a solution was devised to reduce the reaction area of the aluminum by decreasing the surface area of the cell housings. The cell was operable for 128 hours.

Run #13

MACOR sealed with aluminum foil gaskets housed this experiment. Ni electrodes were allowed to go to NiO in-situ. A prepressed disk of $(Li_{0.62}K_{0.38})_2CO_3$ infiltrated the 68% porous self-produced zirconia membrane in-situ. Strong seals developed immediately and held the duration of the experiment.

100% stoichiometric CO_2 removal was observed on the cathode side of the cell prompting H_2S addition. Equilibrium gas compositions consisted of (8.51% CO_2, 23.49% CO, 9.49% H_2O, 58.51% H_2, and 219 ppmv H_2S). A laboratory power failure caused the cell temperature to drop below the electrolyte melting temperature(500°C). Membrane thermal shock ensued creating cracks which allowed extensive hydrogen cross-over. Attempts to restart the cell failed, resulting in shut down after 99 hours.

Run #14

Set-up for run #14 was identical to run #13. Once again strong seals lasted throughout the experiment. A self-produced zirconia membrane, 65% porosity, provided electrolyte support. 100% stoichiometric CO_2 reduction occurred on the cathode side of the cell. H_2S addition ensued. The cell reached equilibrium gas compositions of (8.51% CO_2, 23.49% CO, 9.49% H_2O, 58.51% H_2, and 156 ppm H_2S). Current applied to the cell had no effect in removing H_2S. The assumption of electrode degradation on the cathode side was proven by attempts to transport carbonate, resulting in only 50% stoichiometric removal of CO_2. Figure 2 shows the phase transition region that exists using Ni electrodes with the equilibrium gas contents. Once this transition occurs reactions sites for the reduction of H_2S drastically decline resulting in loss of current efficiency. Another alternative such as cobalt (Figure 3) must be used to provide

adequate pore area for the desired reaction to occur. The cell was shut-down after 98 hours.

Summary

Excellent stability has been shown using the self-produced zirconia membranes. The solution to micro-cracks requires the simple application of back pressure from the anode side of the cell. Aluminum foil gaskets provided excellent seals throughout run #13 & run #14. Current effects of the aluminum foil have yet to be determined, however past use resulted in favorable H_2S removal.

Planned Work for Next Quarter

Work will continue with the self-produced membranes and aluminum foil gaskets. The main focus will be on adequate cathode materials providing the proper reduction area for efficient H_2S removal.

Figure 2 Phase diagram for the Ni-O-S system at 650°C

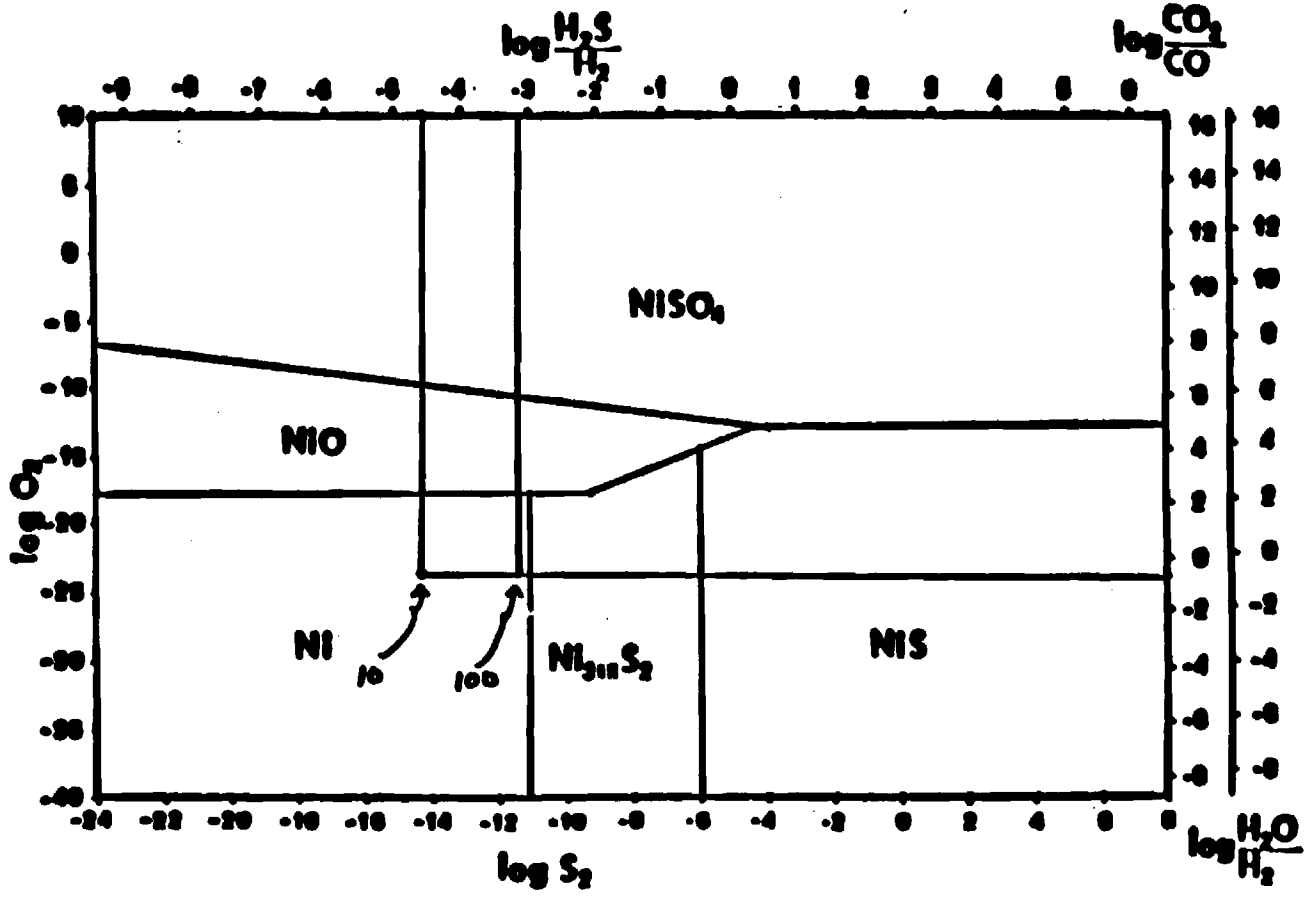
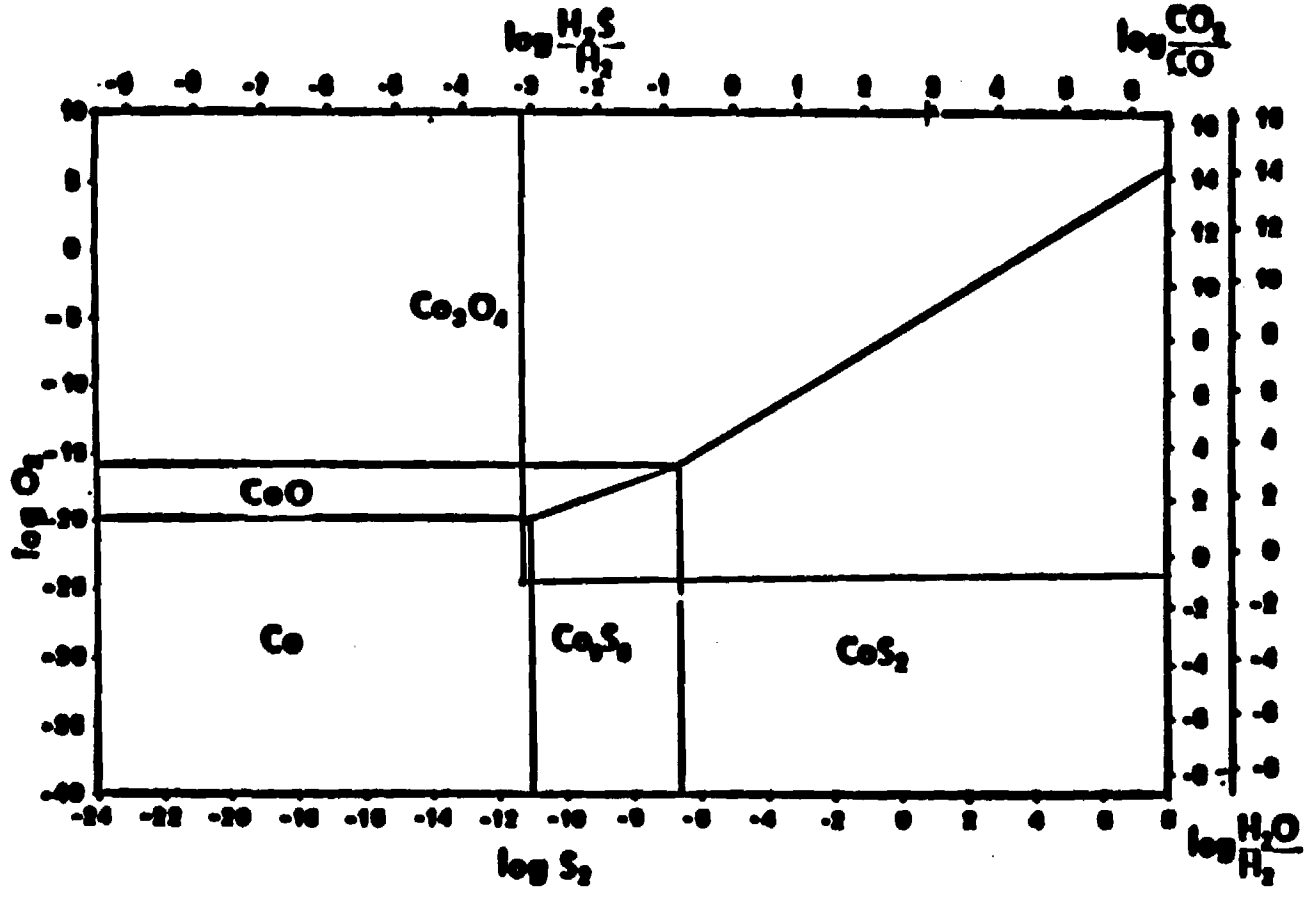


Figure 3 Phase diagram for the Co-O-S system at 650°C



DOE F 1332.16 (10-84)
(Formerly RA-427)

OMB Approval
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1. DOE Report No. 9

2. DOE Contract No. DE-FG22-91PC91288

3. Title High Temperature Electrochemical Separation of H_2S from Coal Gasification Process Streams

4. Type of Document ("x" one)
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   - [ ] b. Conference paper:
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     - Date of conference _____
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   Organization
   Georgia Tech Research Corporation

   Signature [illegible] | Phone (404) 894-2839 | Date 8-2-93

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   - [ ] b. Report has been sent to responsible DOE patent group for clearance.

Quarterly Progress Report:

High Temperature Electrochemical Separation Of H2S from Coal Gasification Process Streams

Grant DE-PS22-91PC91282

April 1, 1993 - June 30, 1993

by

Professor Jack Winnick

Georgia Institute of Technology

School of Chemical Engineering

Atlanta, GA 30332-0100

Objective

A method of polishing coal synthesis gas by an electrochemical operation is being perfected. The operation which takes advantage of an electrochemical potential gradient rather than conventional techniques, removes poisonous H_2S from the coal gas stream leaving only H_2 to enrich the exiting flue gases. Sulfur is the by-product which is carried away by an inert sweep gas and condensed downstream. The technology is attractive due to aesthetics as well as economics when compared to other alternatives.

Experiments this quarter focused on production of cobalt electrodes cable of sustaining pore symmetry in the cell environs.

Introduction

A schematic of the mechanism used for electrochemical separation is presented in Figure 1. The process gas, cleansed of particulates, passes over the cathode. Here the best Lewis acid(electron acceptor), will be reduced. In this case H_2S is favored, resulting in the following:

$$H_2S + 2e^- \rightarrow S^{2-} + H_2$$

The sulfide ions are transported, by current through the membrane. Once the sulfide ion reaches the anode side, oxidation to elemental sulfur occurs by the following:

$$S^{2-} \rightarrow 1/2\ S_2 + 2e^-$$

The vaporous sulfur is condensed downstream.

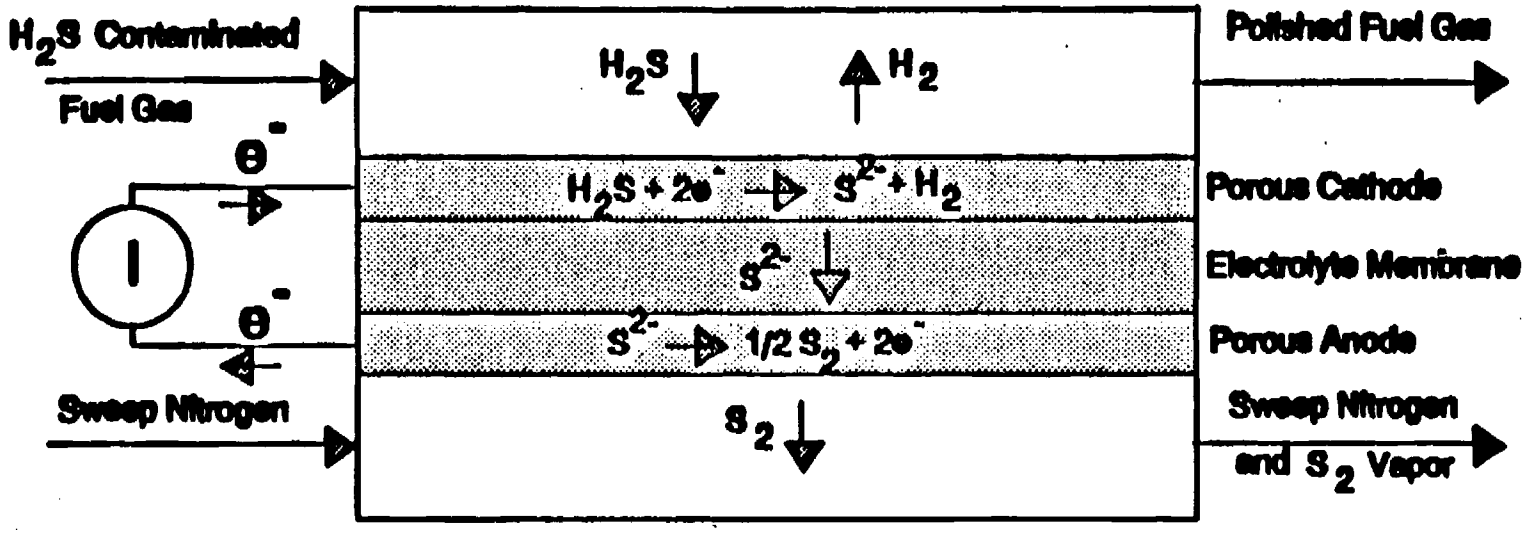


Figure 1.
Electrochemical Fuel Gas Desulfurization Cell.

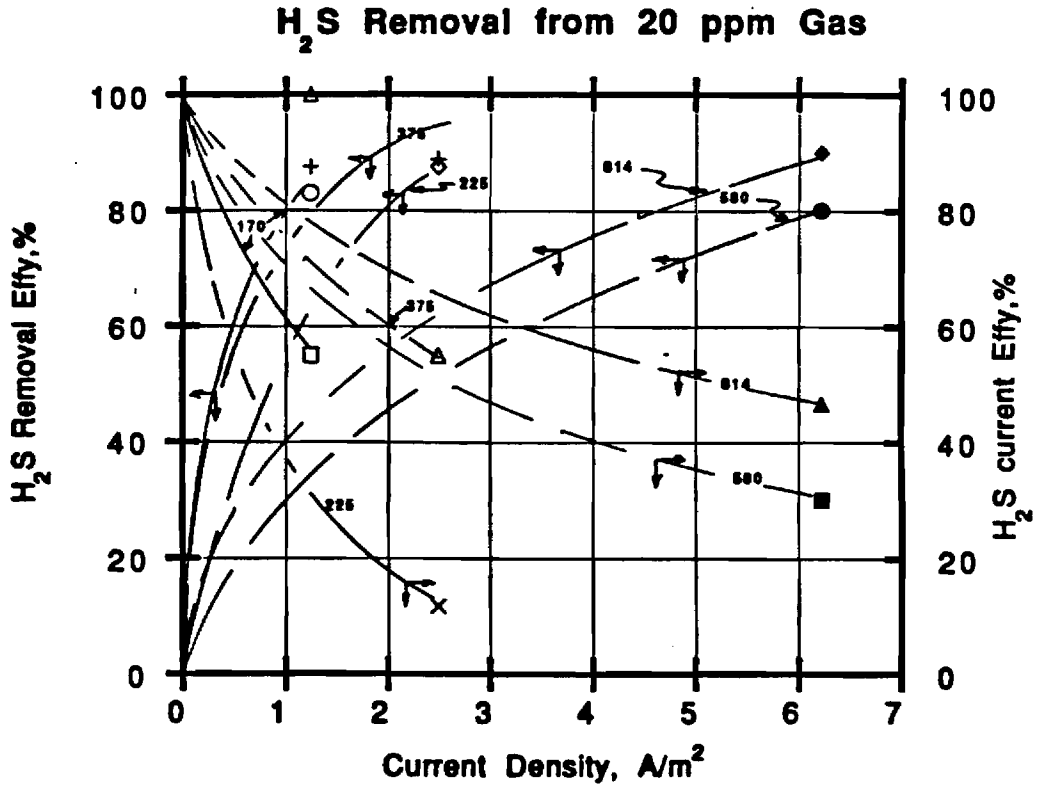
Alternate Cathode Material

Materials used in our electrochemical membrane separator(EMS) replicate molten carbonate fuel cells(MCFC). Process compatibility, once integrated into gasification plants, will exist due to identical set-up as the power application(MCFC). Lithiated nickel electrodes, used in MCFCs, have been tested in our EMS with favorable results. H_2S removal efficiencies over 90%, using inlet H_2S levels of 100ppmv and 20ppmv, were recorded at varying flow rates(170-814cc/min) shown in Figure 2. However, H_2S current efficiencies remained low, notably with 100ppmv inlet H_2S. Recent experiments(#11 - #14) using nickel cathodes and 100ppm inlet H_2S revealed significant reduction in cathode diameter along with enclosure of platinum current collectors. Nickel cathodes in 20ppmv H_2S streams exhibited stable behavior.

Variant nickel cathode behavior with different inlet concentrations can be explained by the Ni-O-S phase diagram at 650°C(experimental temperature). Figure 3, using equilibrium process gas compositions, shows 100ppmv H_2S may react with the nickel cathode to form $Ni_{3+x}S_2$, a conductive molten state. 10 ppmv inlet H_2S equilibrates to NiO, a conductive metal oxide, also in Figure 3.

Phase transition, Ni to $Ni_{3+x}S_2$, is detrimental primarily from loss of reaction sites for H_2S electronation. The high porosity semi-conducting metal transforms to a conductive, molten disk losing all interstitial pore area.

(a)



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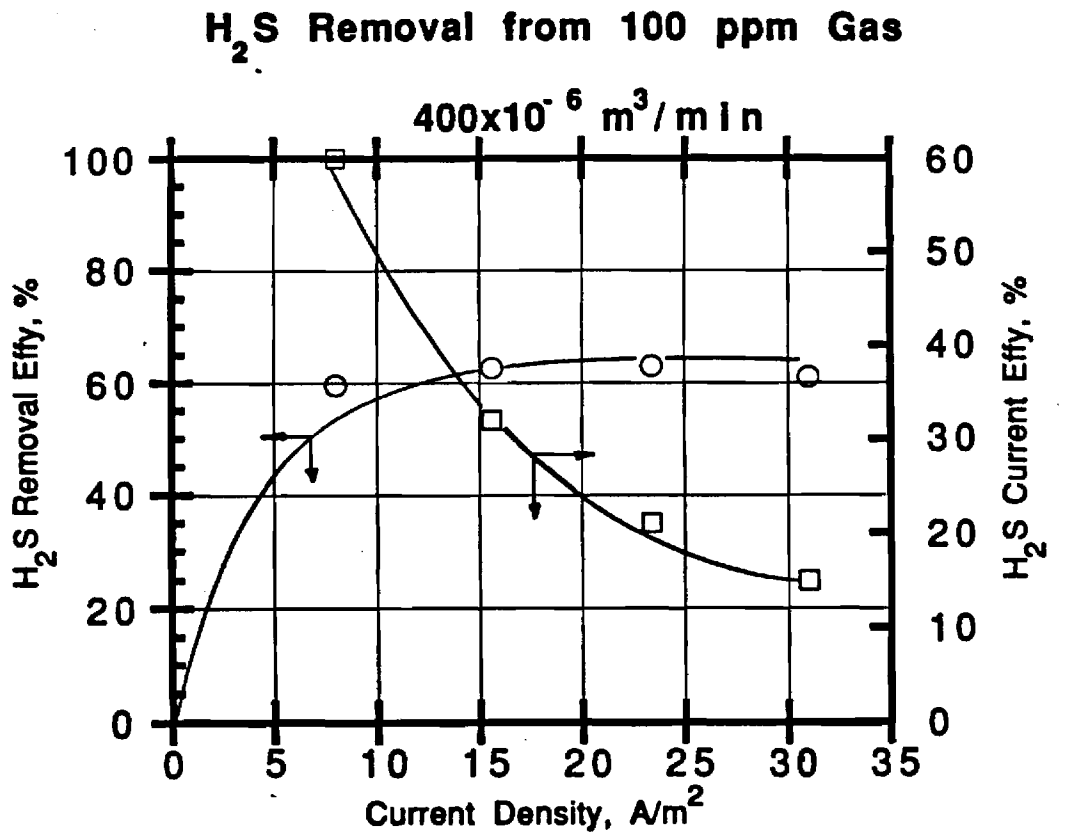


Figure 2 (a) 20ppmv Inlet H_2S, (b) 100ppmv Inlet H_2S

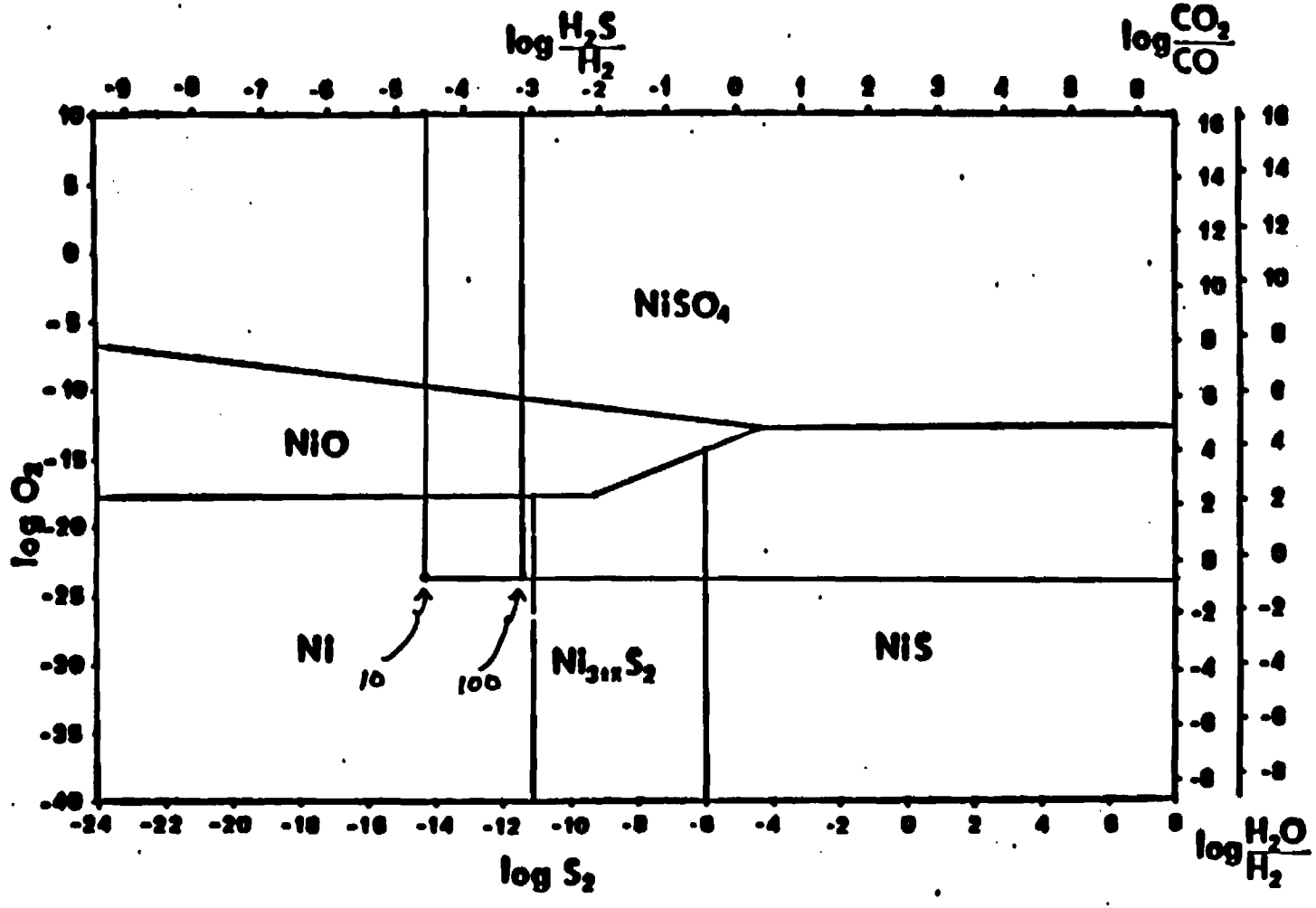


Figure 3 Phase diagram for the Ni-O-S system at 650°C.

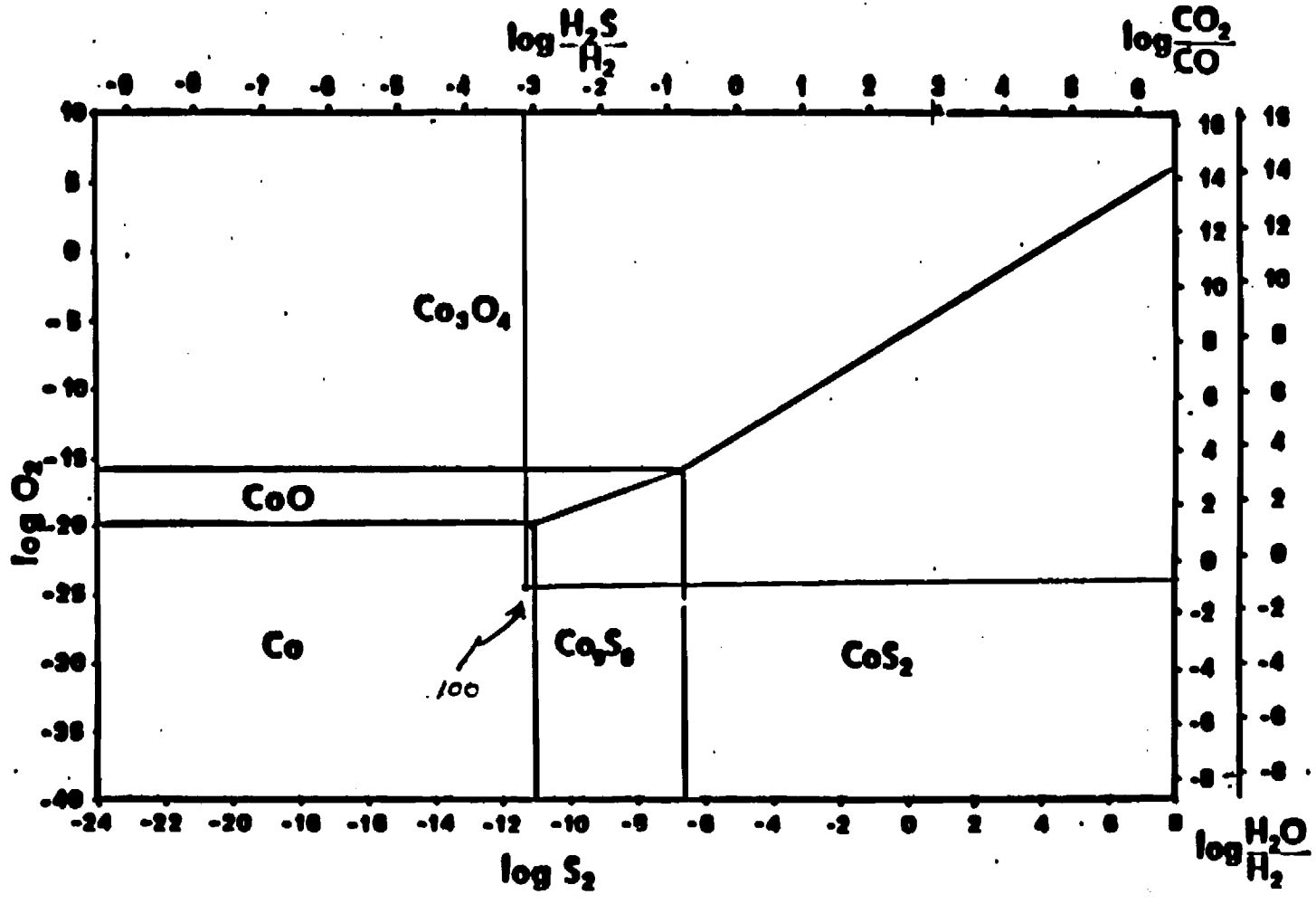


Figure 4 Phase diagram for the Co-O-S system at 650°C.

Only superficial area exists, resulting in zero H_2S surface concentration.

A suitable cathode material stable in the cell environ, must be fabricated to continue 100ppmv experiments. From Figure 4, Co forming Co_9S_8 a conductive metal should perform efficiently. The next step is to develop a Co electrode identical in morphology to the aforementioned nickel cathodes.

Experimental Results

Due to the instability of nickel as a cathode material under conditions of high H_2S concentrations(>100ppmv) alternate materials were investigated. The best material, from past experience and phase stability when using 100ppmv H_2S, is cobalt. Using various methods to replicate previous electrode morphology, eventually produced a >80% porous cobalt electrode, similar in porosity and pore structure to previous nickel cathodes. Scanning electron microscopy(SEM) to investigate pore diameter and in lab test to confirm interconnecting pore channels finalized electrode testing. The necessity of pore size and interconnecting channels derives from the electrode-electrolyte interface where H_2S electronation occurs. Without adequate electrode wetting, by the electrolyte, and the availability of contaminated fuel gas reaching this interface, H_2S removal is not possible.

Initial Electrodes

Initial attempts to replicate electrodes used 2 micron cobalt powder singularly and with a mix of 25 wt% methocel, followed by 149 micron powder singularly and with mixtures of methocel and naphthalene.

I.) Pressing the 2 micron powder without any binding additive provided a cohesive disk, sintered at 800°C. The resulting electrode was completely conductive, but dense(40% porosity) and unusable for efficient H_2S removal.

II.) Pressing a mixture of 2 micron cobalt powder with 25 wt% methocel, in order to increase porosity, then sintering at 800°C in a nitrogen atmosphere provided more favorable results. The electrode was higher in porosity(55%) and conductive, due to the nitrogen atmosphere preventing oxidation to non-conductive cobalt oxide. However, incomplete binder(methocel) burn-out caused a fragmented disk not conducive for efficient electrode material.

III.) Sintering a 3 wt% methocel, 97 wt% 149 micron cobalt powder disk to 1000°C proved unfavorable, attributed to incomplete binder burnout along with incohesive particle structure. The electrode characteristics remain similar to the previous mixture(II) of methocel and 2 micron powder.

IV.) Using pure 149 micron cobalt powder was attempted but difficult due to the larger particle size lacking coherence, once pressed. The disk, sintered to 1100°C in N_2 atmosphere, densified to an unacceptable porosity(50%), similar to the 2 micron powder electrode(I).

V.) Sintering to 1000°C in an oxygen atmosphere using a pressed disk of 2 wt% methocel balance 149 micron cobalt powder, in an attempt to completely burn-out the binder, did not conform. The electrode flaked, prompting another binder alternative, preferably a sublimating substance requiring low temperature phase transition; therefore, releasing without combustion process interference.

VI.) Naphthalene was chosen as a sublimating binder and pressed with 149 micron powder, 1gram to 30grams respectively. The disk, after sintering to 700°C, failed to solidify forming a mound of conductive powder. The predominant problem arose from agglomeration of the naphthalene particles preventing uniform heterogeneity.

First Batch Electrodes

A consortium of mixtures were next attempted given the previous information. The various mixtures used were batch sintered in a nitrogen atmosphere to 1195°C. The temperature increase generated more particle interaction due to the

proximity of cobalt's melting temperature(1492°C). Nine different disk were pressed each varying in components as follows:

1) Pure 2 micron cobalt powder
2) 3wt% methocel balance 2 micron powder
3) 12wt% methocel balance 2 micron powder
4) 56wt% methocel balance 2 micron powder
5) 16wt% naphthalene balance 2 micron powder
6) 30wt% 2 micron powder 70wt% 149 micron powder
7) 8wt% methocel balance 149 micron cobalt powder
8) 6wt% naphthalene balance 149 micron powder
9) Pure 149 micron cobalt powder

with 4 providing favorable results. The mixture(4) densified to 2.36 g/cm^3 with a porosity of 75%. Next investigation shifted to other major concerns, aforementioned pore diameter and interconnecting channels. Without the previous two criteria lack of reaction sites for H_2S electronation results in unfavorable current efficiencies. After SEM pictures, Figure 5, showed pore size acceptability(compared to previous electrodes) and electrode bubble testing proved interconnecting channels existed, other test incorporating high wt% binding materials followed.

Second Batch

Success with high wt% methocel, resulted in test mixtures, sintered conditionally identical as follows:

1) 63wt% methocel balance 2 micron powder
2) 40wt% methocel 15wt% 2 micron 65wt% 149 micron
3) 55wt% hydroxyethylcellulose balance 2 micron
4) 64wt% methocel balance 149 micron powder
5) 43wt% methocel balance 149 micron powder
6) 23wt% methocel balance 149 micron powder
7) 20wt% hydroxyethylcellulose balance 149 micron

1, with similar component make up as 4, densified to 1.998 g/cm^3 with high conductivity. Favorable porosity(78%) and disk morphology from Figure 5 provided proof of an electrode solution.

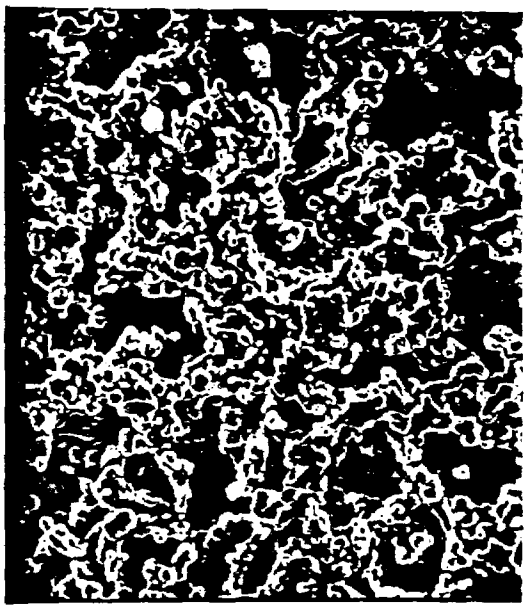
Summary

Fabrication of electrodes similar to previous nickel electrodes were produced using a mixture of ~60wt% methocel with the balance 2 micron cobalt powder. Two large diameter disk sintered component and condition similar have been developed with promising results.

Planned Work for Next Quarter

Work will continue with the self-produced membranes and aluminum foil gaskets from previous quarter experiments. The main focus will be on H_2S current efficiency using the fabricated cobalt cathodes with 100ppmv H_2S fuel gas.

(a)



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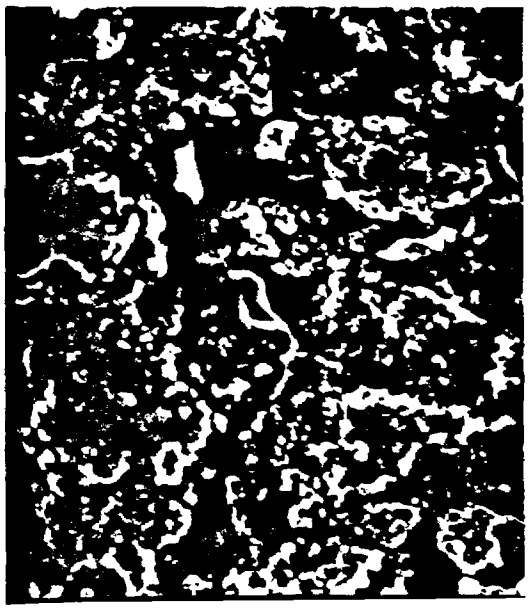

(c)

Figure 5 (a) Previous Ni cathode, (b) #4 first batch, (c) #1 second batch

DOE F 1332.16 (10-84)
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   Signature: X
   Phone: (404) 894-2839
   Date: 11/9/93

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Quarterly Progress Report:

High Temperature Electrochemical Separation Of H2S from Coal Gasification Process Streams

Grant DE-PS22-91PC91282

July 1, 1993 - September 30, 1993

by

Professor Jack Winnick

Georgia Institute of Technology

School of Chemical Engineering

Atlanta, GA 30332-0100

Objective

A method of polishing coal synthesis gas by an electrochemical operation is being perfected. The operation that takes advantage of an electrochemical potential gradient rather than conventional techniques, removes poisonous H_2S from the coal gas stream leaving only H_2 to enrich the exiting flue gases. Sulfur is the by-product that is carried away by an inert sweep gas and condensed downstream. The technology is attractive due to aesthetics as well as economics when compared to other alternatives.

Experiments this quarter focused on removing 100 ppmv inlet H_2S, utilizing laboratory fabricated cobalt cathodes.

Introduction

A schematic of the mechanism used for electrochemical separation is presented in Figure 1. The process gas, cleansed of particulates, passes over the cathode. Here the best Lewis acid, electron acceptor, will be reduced. In this case H_2S is favored, resulting in the following:

$$H_2S + 2e^- \rightarrow S^{2-} + H_2$$

The sulfide ions are transported, by current, through the membrane. Once the sulfide ion reaches the anode side, oxidation to elemental sulfur occurs by the following:

$$S^{2-} \rightarrow 1/2\ S_2 + 2e^-$$

The vaporous sulfur is condensed downstream.

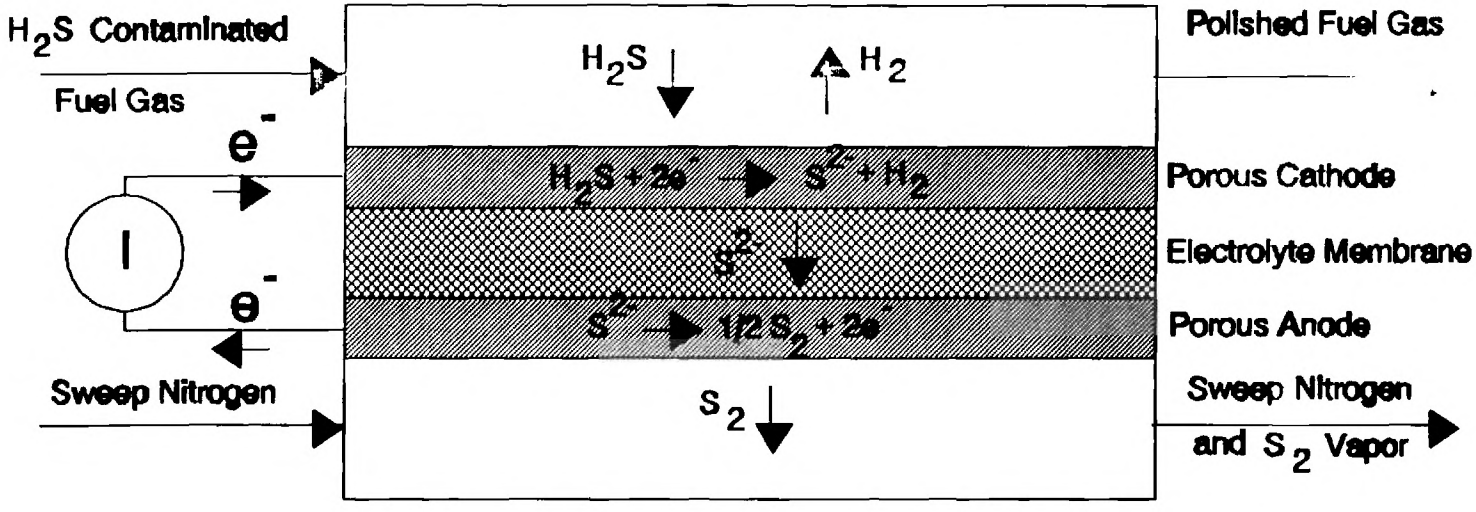


Figure 1. Conceptual Electrochemical Removal Cell

Alternate Cathode Material

Materials used in our electrochemical membrane separator(EMS) replicate molten carbonate fuel cells(MCFC). Process compatibility, once integrated into gasification plants, will exist due to identical set-up as the power application(MCFC). Lithiated nickel electrodes, used in MCFCs, have been tested in the EMS with favorable results. H_2S removal efficiencies over 90%, using inlet H_2S levels of 100ppmv and 20ppmv, were recorded at varying flow rates(170-814cc/min). However, H_2S current efficiencies remained low, notably with 100ppmv inlet H_2S. Recent experiments(#11 - #14) using nickel cathodes and 100ppm inlet H_2S revealed significant reduction in cathode diameter along with enclosure of platinum current collectors. Nickel cathodes in 20ppmv H_2S streams exhibited stable behavior.

Variant nickel cathode behavior with different inlet concentrations can be explained by a phase transition at 650°C(experimental temperature). Equilibrium process gas compositions, with >100ppmv inlet H_2S may react with the nickel cathode to form $Ni_{3+x}S_2$, a conductive molten state. Ten ppmv inlet H_2S equilibrates to NiO, a conductive metal oxide.

Phase transition, Ni to $Ni_{3+x}S_2$, is detrimental primarily from loss of reaction sites for H_2S electronation. The high porosity, semi-conducting metal transforms to a conductive, molten disk losing interstitial pore area. Predominantly superficial area exists, resulting in smaller

electronation area, creating the necessity of higher current densities for H_2S removal. The problem of Ni phase transition, in the presence of high concentrations of H_2S, had its genesis in the early MCFC experiments using NiO electrodes. The solution was a conversion to cobalt electrodes; however, present MCFC's operate efficiently only with H_2S levels below 1ppmv, alleviating the problem.

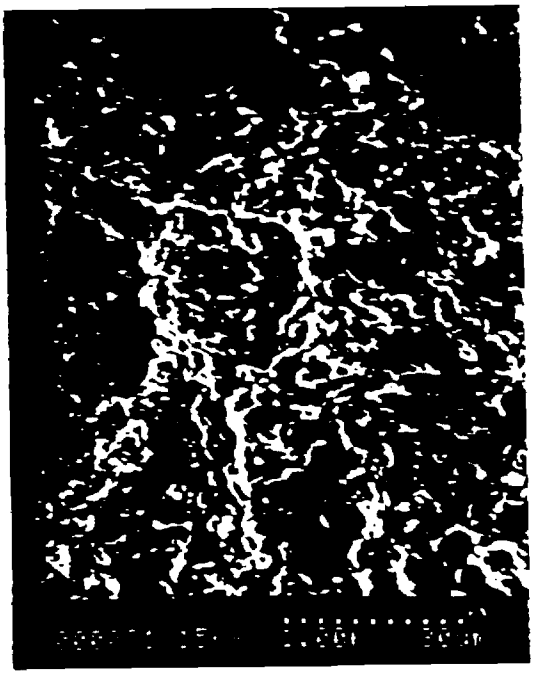
A suitable cathode material stable in the removal environ, fabricated to continue 100ppmv experiments, Co forming Co_9S_8 (a conductive ceramic), performed efficiently. Experimental H_2S removal results utilizing the fabricated cobalt cathode follow.

Experimental Results

Due to the instability of nickel as a cathode material under conditions of high H_2S concentrations(>100ppmv) alternate materials were investigated. The best material, from experience and phase stability when using 100ppmv H_2S, is cobalt. Using various methods to replicate previous electrode morphology, eventually produced a >80% porous cobalt electrode, similar in porosity and pore structure to previous nickel cathodes. Scanning electron microscopy(SEM), Figure 2, to investigate pore diameter and in lab test to confirm interconnecting pore channels finalized electrode testing. The necessity of pore size and interconnecting channels derives from the electrode-electrolyte interface where H_2S electronation occurs. Without adequate electrode

wetting, by the electrolyte, and the availability of contaminated fuel gas reaching this interface, H_2S removal is not possible.

a)



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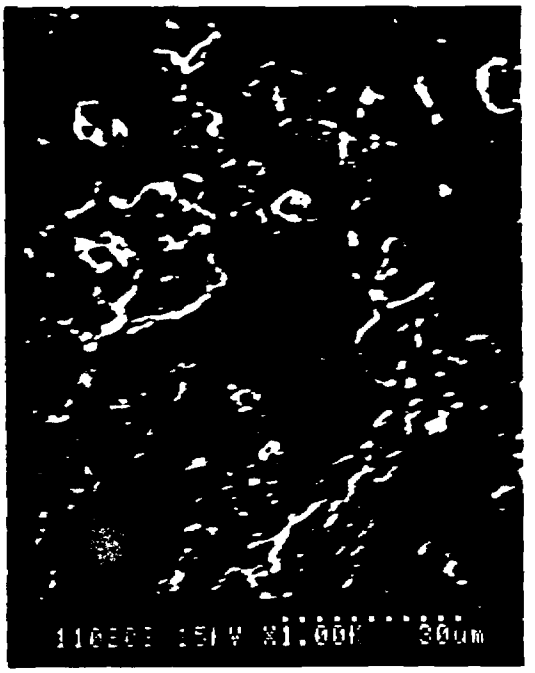

Figure 2. a) Lithiated Ni anode and b) Co cathode

An experiment(Run#15) examining the removal capability of the EMS with cobalt cathode was performed this quarter. The focus dealt with H_2S removal along with H_2S current efficiency using inlet H_2S greater than 100ppmv.

Run#15

Cell materials consisted of a cobalt cathode, the anode material remained $Li_xNi_{1-x}O$, a stabilized zirconia membrane, housings of MACOR(machineable ceramic), aluminum foil gasket seals, and a prepressed disk of $(Li/K)_2CO_3$(6grams) corresponding to the void volume in the zirconia membrane. Examination of the cobalt-cathode EMS, produced stoichiometric CO_2 removal and addition at both cathode and anode, respectively, before addition of H_2S. After introducing H_2S to the EMS system, equilibration to 120ppmv H_2S occurred before applying current. H_2S removal at varying currents was attempted, starting with stoichiometric current(3mA for a flow of 150 cc/min), and increasing to 200mA. H_2S removal did not appear significant(< 10ppmv), with continued stoichiometric CO_2 removal at the cathode and production at the anode. Other concerns were high internal resistance(4 to 6 Ohms) as well as addition of electrolyte(> 10grams, 40% more than initially calculated).

Minimal H_2S removal at varying currents, resulted from three possible reasons:

1) The cathode pore diameter was too small, causing pores to be flooded by electrolyte drawn from

the membrane. In other words, the capillary forces from the cathode were stronger than those of the membrane due to smaller pore diameter in the cathode. Mass transfer would be inhibited, due to slower diffusion through the molten electrolyte filled pores to the electrode surface, instead of typical gaseous diffusion to the electrode surface. This possibility seemed unlikely due to stoichiometric CO_2 removal along with post-mortem examination of the electrode, Figure 2, revealing unflooded and intact pores.

2) Mechanical breakdown in the current carriers. High internal resistance throughout the experiment created concern of faulty circuitry, but post-run analysis proved negative.

3) Micro-cracks in the membrane that would enable hydrogen to cross from the process gas side(cathode side) to the sweep side(anode side). If hydrogen cross-over occurs, two reactions are possible at the anode. One reaction is the oxidation of hydrogen and the sulfide ion to hydrogen sulfide.

$$H_2 + S^{2-} \rightarrow H_2S + 2e^-$$

Anode exit gases checked by gas chromatography showed no evidence of H_2S. The other possible reaction is the oxidation of hydrogen and carbonate to water and carbon dioxide.

$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$$

However, condensation of water was not evident, although low current levels(5mA) produces only 0.05% water in a flow rate of 70 cc/min on the anode side.

The second oxidation reaction, causing loss of carbonate from the electrolyte, induces the favorability of carbonate reduction at the cathode over H_2S due in part to the higher pressure of CO_2 and H_2O available at the cathode(order of 10^5 higher than H_2S) promoting the parasitic reaction.

Favored: $H_2S + 2e^- \rightarrow H_2 + S^{2-}$

Competing: $H_2O + CO_2 + 2e^- \rightarrow CO_3^{2-} + H_2$

Electrolyte loss

The high internal resistance experienced in run#15 corresponds to electrolyte reduction due to formation of process-gas seals. The aluminum foil gaskets, placed on both sides of the membrane between the membrane and outer edge of the housings(outside the electrode well), initially oxidizes in the cell environ at elevated temperatures forming the non-conductive oxide alumina(Al_2O_3). Upon formation of alumina the conversion to $LiAlO_2$ by reaction with lithium carbonate present in the electrolyte occurs. Loss of lithium carbonate, the more conductive of the electrolytic species(more conductive than potassium carbonate), occasions

an increase in resistance throughout the membrane. Therefore continued addition of electrolyte is necessary until complete system equilibrium is attained.

Proof of the formation of other aluminate species was evidenced when post-mortem analysis revealed a blue tint around the cathode side of the EMS. Research revealed that $CoAl_2O_4$(cobalt aluminate) is a bluish color(Thenard's blue), the only of the possible Co reactions found to coordinate.

Summary

The cobalt cathode used in the EMS proved stable and efficient. Removal of H_2S was deterred by the possibility of hydrogen cross-over from process gases creating alternate reactions unfavorable to the removal system. Application of back pressure from the anode side of the cell would be the simplest solution to H_2 cross-over. Examination of water vapor in the anode exit gases would provide proof of the aforementioned reaction hypothesis. Cobalt aluminate formation should not prove problematic, since degradation of the Co cathode did not occur as a result. Once equilibrium is reached electrolyte addition is not necessary, therefore not a major concern.

Planned Work for Next Quarter

Work will continue with the Zirconia membranes and aluminum foil gaskets from previous quarter experiments. The main focus will be on H_2S current efficiency using the fabricated cobalt cathodes with 100ppmv H_2S fuel gas and preventing alternate reactions due to hydrogen cross-over. Initial test of anode gas water vapor content should indicate the actual reaction mechanism.

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Quarterly Progress Report:

High Temperature Electrochemical Separation Of H2S from Coal Gasification Process Streams

Grant DE-PS22-91PC91282

October 1, 1993 - December 31, 1993

by

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Objective

A method of polishing coal synthesis gas by an electrochemical membrane operation is being perfected. The operation takes advantage of an electrochemical potential gradient rather than conventional techniques, separating the H_2S from the coal gas stream, leaving only H_2 to enrich the exiting fuel gases. Sulfur is the by-product that is carried away by a separate inert sweep gas and condensed downstream. The technology is attractive due to simplicity as well as economics when compared to alternatives.

An analytical model describing the preferred reduction of H_2S, the transport of S^{2-}, and the competing transport of CO_3^{2-} through the removal cell has continued. The main objective is the relation between cell polarization and current efficiency. This has been realized.

Experiments this quarter focused on removing 100 ppm inlet H_2S, utilizing laboratory fabricated cobalt cathodes.

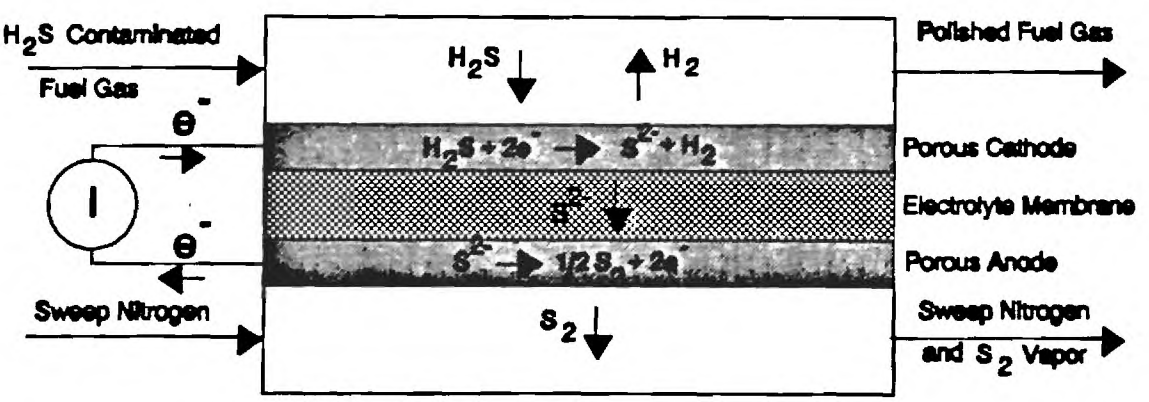


Figure 1. Conceptual Electrochemical Removal Cell

Introduction

A schematic of the mechanism used for electrochemical separation is presented in Figure 1. The process gas, cleansed of particulates, passes over the cathode. Here the best Lewis acid, electron acceptor, will be reduced. In this case H_2S is favored, resulting in the following:

$$H_2S + 2e^- \rightarrow S^{2-} + H_2 \qquad (1)$$

The sulfide ions are transported, by migration and diffusion, across the membrane. Once the sulfide ion reaches the anode side, oxidation to elemental sulfur occurs by the following:

$$S^{2-} \rightarrow 1/2\ S_2 + 2e^- \qquad (2)$$

The vaporous sulfur is condensed downstream.

Processes to remove H_2S typically rely on low-to -ambient temperature adsorption, followed by sorbent regeneration and Claus plant treatment for conversion of H_2S to a salable by-product, sulfur. Although effective, this type of removal is very process-intensive as well as energy-inefficient due to low temperature operation. Gasification streams generally range from 500°C - 1000°C, requiring cooling before and reheating after process gas sweetening. Although these technologies have proven capable of meeting H_2S levels required by MCFC, there are several disadvantages inherent to these processes[7,8].

Alternative high temperature methods are presently available, but process drawbacks including morphological changes in catalytic beds[9] or inefficient molten salt sorbent processes[10] negate savings incurred through energy efficient removal temperatures.

An electrochemical membrane separation system for removing H_2S from coal gasification product streams is the subject of this investigation. The high operating temperature, flow-through design, and capability of selective H_2S removal and direct production of elemental sulfur offered by this process provide several advantages over existing and developmental H_2S removal technologies. The remaining factor is a thorough economic evaluation asserting the viability of the process.

An initial economic evaluation[11] showed the process noteworthy. Further analysis will require developing an analytical model describing 1) the preferred reduction of H_2S among competing reactants in the gasification stream, 2) the transport of S^{2-} through the electrolyte filled membrane, and 3) competing transport of CO_2 through the removal cell. The model can give the maximum current efficiency for H_2S removal, depending on variables such as flow rate, temperature, current application, and total cell potential. Extended application of the model will predict cell performance under varying cell currents, gas compositions and flow rates. It will also permit economic projection in various applications.

Analytical Model

A theoretical model based on applied current, flow rate, and electrochemical effects has been investigated, relating anode CO_2 production with % H_2S removal. Although the model is not completed, adequate power estimates for percentage removals of H_2S can be computed.

Preferential Reduction of H_2S

H_2S has been shown to be readily reduced in hot gas mixtures, even at low ppm levels. The situation is complicated when coal gas mixtures are processed. Carbon dioxide and water vapor compete in the reduction reaction at the cathode by:

$$CO_2 + H_2O + 2e^- \Rightarrow CO_3^{2-} + H_2 \quad (3)$$

The ionic flux through the membrane depends on the relative mobility of carbonate and sulfide ions as well as their concentrations.

Preventing the oxidation of carbonate at the anode is necessary for prohibiting its transport through the membrane, the desired anodic reaction being:

$$S^{2-} \Rightarrow 1/2\ S_2 + 2e^- \quad (2)$$

This occurs at a standard potential some 700 mV lower than the oxidation of carbonate:

$$CO_3^{2-} \Rightarrow CO_2 + 1/2\ O_2 + 2e^- \quad (4)$$

Summing the half-cell reactions (1) and (2) results in the following overall reaction at 923K:

$$H_2S \Leftrightarrow H_2 + 1/2\ S_2 \qquad E_a^o = -0.239\ V \quad (5)$$

and when the half-cell reactions (3) and (4) are summed:

$$H_2O \Leftrightarrow H_2 + 1/2\ O_2 \qquad E_b^o = -1.030\ V \quad (6)$$

The relative extent of each of these reactions is determined by chemical equilibrium. Each will occur at the *same cell potential;* but as expressed by the Nernst relation, the concentration terms will be greatly affected by the large difference in the standard cell potentials, E^o, values.

$$E = E_a^o - \left(\frac{RT}{nF}\right)\ln\left\{\frac{a_{S^{2-}_{cath}} P_{H_2\ cath} P^{\frac{1}{2}}_{S_2\ an}}{a_{S^{2-}_{an}} P_{H_2S_{cath}}}\right\} \quad (7)$$

$$E = E_b^o - \left(\frac{RT}{nF}\right)\ln\left\{\frac{a_{CO^{2-}_{3\ cath}} P_{H_2\ cath} P_{CO_2\ an} P^{\frac{1}{2}}_{O_2\ an}}{a_{CO^{2-}_{3\ an}} P_{CO_2\ cath} P_{H_2O_{cath}}}\right\} \quad (8)$$

We here assume a process gas is supplied to the cathode with an H_2S level of 100 ppmv, a CO_2 level of 14.2%, and an H_2O level of 5.7%, and that 90% of the H_2S is to be removed via reaction (1). There exists an activity ratio of $\frac{a_{CO_3^{2-}}}{a_{S^{2-}}}$ on the order of 10^5 in the anolyte, assuming equivalent electrode kinetics[5,6] for the two reactions, before a significant amount (e.g. 1%) of the carbonate is oxidized. When compared to the activity ratio of $\frac{a_{CO_3^{2-}}}{a_{S^{2-}}}$ in the catholyte of 3000, this shows the huge thermodynamic preference for the oxidation of S^{2-} to elemental sulfur by equation (2).

The net effect, under these conditions, is continuous and selective removal of H_2S from the process gas accompanied by enrichment of the process gas with H_2 and direct generation of elemental sulfur at the anode.

Electrical Power Requirements

The power to drive the electrochemical membrane separator is a direct function of the potential required to drive the removal cell multiplied by the current carried by the sulfide ions across the membrane.

$$\text{Power} = (\text{Cell Potential}) * (\text{Cell Current}) \qquad (9a)$$

Estimation of the current carried by the removal cell is straight-forward since two faradays of charge are carried by each mole of sulfide transported (or each mole of H_2S removed). Calculation of the cell potential is outlined below.

Along with the Nernst relation, additional energy is required to operate the separation cell due to irreversible losses. These losses occur by internal resistance, concentration effects in the process gases, and the activation barrier for electron transfer. The result is the total cell potential increasing over the reversible potential[1].

Ohmic Polarization:

Ohmic losses occur due to resistance in ionic and electronic transfer of current through the separation system. The ohmic losses can be expressed by:

$$\eta_{ohm} = IR \tag{9}$$

with **I** representing current and **R** the total cell resistance.

Concentration Polarization

Concentration polarization originates from developing concentration gradients due to consumption of electro-active species at the electrode surface. Transport of these species is composed of four steps, occurring in series: 1) the H_2S must diffuse through the gas-phase boundary layer to the cathode interface, 2) it must diffuse through the pores of the electrode to the electrolyte film, 3) the sulfide ion must migrate to the anode, and 4) the oxidized species must diffuse out into the sweep gas at the anode. The effect of step 3 has been minimized due to proper membrane design and steps 2 and 4 have been found to be of no consequence[2]. The limiting process for removal is thus diffusion of electro-active species to the electrode pores from the bulk gas. Since the gas-phase concentration of H_2S changes along the length of the channels, a log-mean average is used in the calculation of limiting current density by:

$$i_L = nFk_m\rho \frac{\left(y_{inlet} - y_{exit}\right)}{\ln\left(\frac{y_{inlet}}{y_{exit}}\right)} \tag{10}$$

where **n** is the number of electrons transferred per mole of species removed, **F** is

Faraday's constant, k_m is mass transfer coefficient, ρ is the molar density of the bulk gas, and y_x is the inlet and exit mole fraction of H_2S. The average mass transfer coefficient was derived from an estimated Sherwood number dependent on channel dimension and constant H_2S surface concentration[3] given by:

$$N_{Sh} = \frac{k_m D_{eq}}{D_{ab}} \tag{11}$$

with D_{eq} defined as the equivalent channel diameter above the electrode surface:

$$D_{eq} = 4r_h = \frac{4(\text{cross} - \text{sectional area})}{(\text{wetted perimeter})} \tag{12}$$

and D_{ab} the diffusion coefficient of H_2S through the predominant species by volume in the bulk according to[4]:

$$D_{ab} = \frac{0.0018583T^{\frac{3}{2}}}{P\sigma_{ab}\Omega_{D_{ab}}}\sqrt{\frac{1}{M_a} + \frac{1}{M_b}} \tag{13}$$

therefore, concentration overpotential is expressed in terms of applied current by:

$$\eta_{conc} = \frac{RT}{nF}\ln\left(1 - \frac{i}{i_l}\right) \tag{14}$$

Activation Polarization:

The activation polarization at both cathode and anode is related to the rates of electrochemical reactions occurring at these electrodes. The

expression relating the kinetics of these electrode reactions is the Butler-Volmer equation:

$$i = i_o\left[\exp\left(\frac{\alpha_a F\eta_{act,a}}{RT}\right) - \exp\left(\frac{-\alpha_c F\eta_{act,c}}{RT}\right)\right] \tag{15}$$

which holds for specified temperature, pressure, and concentration of reacting species. The transfer coefficients α_a and α_c sum to the number of electrons transferred in the reaction:

$$\alpha_a + \alpha_c = n \tag{16}$$

Cell Voltage:

Total cell voltage incorporating *ohmic, concentration,* and *activation* overpotentials along with the Nernstian effects (7) sums to:

$$V_{cell} = \Delta E_{c-a} - |\eta_{conc}| - |\eta_{act}| - \eta_{ohmic} \tag{17}$$

where ΔE_{c-a} is the total cathode-to-anode cell voltage.

The results exhibited in Table I, II, and III were generated using this analytical approach. The run conditions assumed equal cathodic and anodic flow rates of (200 cc/min) (the calculated results are independent of anode sweep gas flow rate), atmospheric system pressure, a run temperature of 650 ^{o}C, and three order of magnitude changes in H_2S removal (1000 ppm to 1 ppm). The cathodic and anodic exchange current densities were estimated at 40 mA/cm^2 after the results of the free electrolyte studies[5,6]. The exchange coefficients, α_a and α_c, were assumed to be unity. Ohmic resistance across the cell was

conservatively estimated to be 1 Ω, based on Molten Carbonate Fuel Cell (MCFC) results[1].

Table I. Predicted Cross-cell Potential with H_2S Removal; 1000 ppm Inlet

Removal	E_{c-a} (V)	Ohm. (V)	Conc. (V)	$Act._c$ (V)	$Act._a$ (V)	Total (V)
10%	-0.2783	-0.0026	-0.00039	-0.000284	0.000284	-0.2819
20%	-0.2968	-0.0052	-0.00083	-0.000569	0.000569	-0.3039
30%	-0.3101	-0.0078	-0.00133	-0.000853	0.000853	-0.3210
40%	-0.3220	-0.0104	-0.00192	-0.001137	0.001137	-0.3367
50%	-0.3337	-0.0130	-0.00263	-0.001421	0.001421	-0.3521
60%	-0.3462	-0.0156	-0.00352	-0.001706	0.001706	-0.3687
70%	-0.3607	-0.0182	-0.00469	-0.001990	0.001990	-0.3875
80%	-0.3795	-0.0208	-0.00641	-0.002274	0.002274	-0.4112
90%	-0.4094	-0.0234	-0.00952	-0.002558	0.002558	-0.4474

Table II. Predicted Cross-cell Potential with H_2S Removal; 100 ppm Inlet

Removal	E_{c-a} (V)	Ohm. (V)	Conc. (V)	$Act._c$ (V)	$Act._a$ (V)	Total (V)
10%	-0.3241	-0.00026	-0.00039	-.0000284	.0000284	-0.3248
20%	-0.3425	-0.00052	-0.00083	-.0000569	.0000569	-0.3440
30%	-0.3559	-0.00078	-0.00133	-.0000853	.0000853	-0.3582
40%	-0.3678	-0.00104	-0.00192	-.0001137	.0001137	-0.3710
50%	-0.3795	-0.00130	-0.00263	-.0001421	.0001421	-0.3837
60%	-0.3920	-0.00156	-0.00352	-.0001706	.0001706	-0.3974
70%	-0.4065	-0.00182	-0.00469	-.0001990	.0001990	-0.4134
80%	-0.5252	-0.00208	-0.00641	-.0002274	.0002274	-0.4342
90%	-0.4551	-0.00234	-0.00952	-.0002558	.0002558	-0.4675

Table III. Predicted Cross-cell Potential with H_2S Removal; 10 ppm Inlet

Removal	E_{c-a} (V)	Ohm. (V)	Conc. (V)	Act.$_c$ (V)	Act.$_a$ (V)	Total (V)
10%	-0.3699	-0.000026	-0.00039	-.0000028	.0000028	-0.3703
20%	-0.3883	-0.000052	-0.00083	-.0000056	.0000056	-0.3892
30%	-0.4017	-0.000078	-0.00133	-.0000085	.0000085	-0.4031
40%	-0.4135	-0.000104	-0.00192	-.0000113	.0000113	-0.4156
50%	-0.4252	-0.000130	-0.00263	-.0000142	.0000142	-0.4280
60%	-0.4377	-0.000156	-0.00352	-.0000170	.0000170	-0.4414
70%	-0.4522	-0.000182	-0.00469	-.0000199	.0000199	-0.4571
80%	-0.4710	-0.000208	-0.00641	-.0000227	.0000227	-0.4777
90%	-0.5009	-0.000234	-0.00952	-.0000255	.0000255	-0.5107

These results show the activation overpotentials at both cathode and anode are negligible. This shows extremely rapid electrochemical kinetics as compared to diffusion effects from the bulk gas phase and through the electrolyte filled membrane. Cross-cell potentials are shown as the sum of the Nernstian, concentration, and ohmic polarization effects. Therefore, at 90% removal H_2S (1000 ppm - 100 ppm; 100 ppm - 10 ppm; 10 ppm to 1 ppm), the data of Table I, II, and III show total cross-cell potentials of -0.4474 V, -0.4675 V, and -0.5107 V, which agree well with experimental cross-cell potentials. Total power requirements for these removals from **(9a)** are 10.5 W, 1.09 W, and 0.12 W (not considering current loss from anodic CO_2 production).

Parallel Sulfide, Carbonate Transport

Since the carbonate transport of reaction (6) parallels the sulfide transport of reaction (5), the same current is available for transport of both species. Therefore, only a certain amount of current will act to transport either constituent giving a finite maximum current efficiency with respect to H_2S removal for any percentage of H_2S removed. This is dependent on gas composition and total cross-cell potential required for the desired separation of H_2S. Once the total cross-cell potential is calculated for the desired H_2S removal, the Nernst expression for transport of carbonate (8) can be equated to this value, since the relative extent of each occur at the same potential. The extent of parasitic CO_2 current from the removal cell associated with %H_2S removal is shown in Figure 2, 3, and 4.

Examination of the results shows that H_2S current efficiency drops only to 99.5% at 90% H_2S removal (1000 ppm to 100 ppm H_2S), 93.2% at 90% H_2S removal (100 ppm to 10 ppm H_2S), and 40.2% at 90% H_2S removal (10 ppm to 1 ppm H_2S). The excess current goes to produce anodic CO2.

This is a favorable result considering the power requirement at higher inlet H_2S concentrations is considerably greater than at lower concentrations, Figure 5 (10.52 W at 1000 ppm inlet H_2S, 0.29 W at 10 ppm inlet H_2S); a high efficiency is a must in the higher H_2S concentrations if the process is to be economically viable. Energy requirements for the 10 ppm H_2S removal are negligible, shown in Figure 5, alleviating concern due to lower current efficiencies.

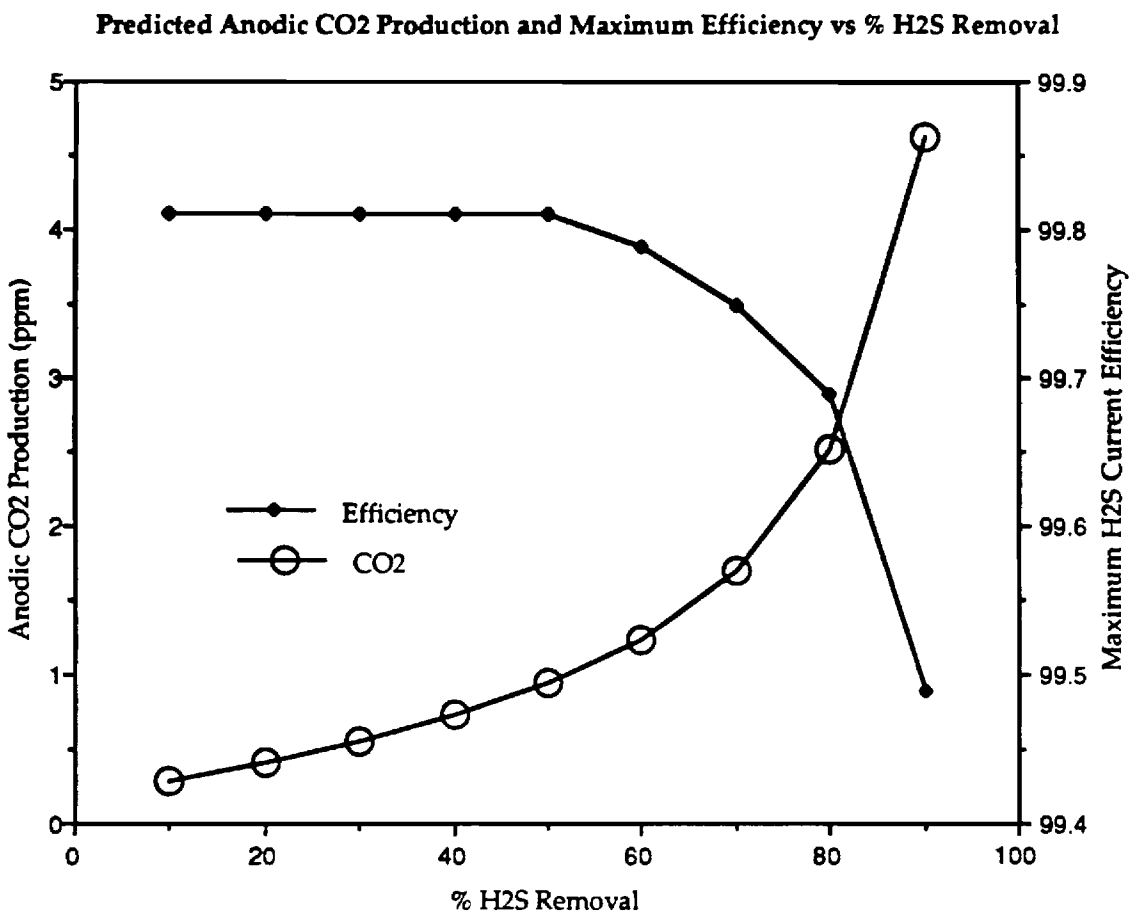


Figure 2. 1000 ppm inlet H_2S

Experimental Results

An experiment (Run#16) examining the removal capability of the EMS with cobalt cathode was performed this quarter. The focus dealt with H_2S removal as well as containing hydrogen cross-over from the process gas side (cathode) of the membrane to the sweep gas side (anode).

Run#16

Cell materials consisted of a cobalt cathode (80% porous), the anode material remained Ni (85% porous), a stabilized zirconia membrane (66% porous), housings of MACOR (machineable ceramic), aluminum foil gasket seals, and a prepressed disk of $(Li/K)_2CO_3$ (8 grams) corresponding to the void

volume in the zirconia membrane. Electrode materials were verified by x-ray diffraction, Figure 6.

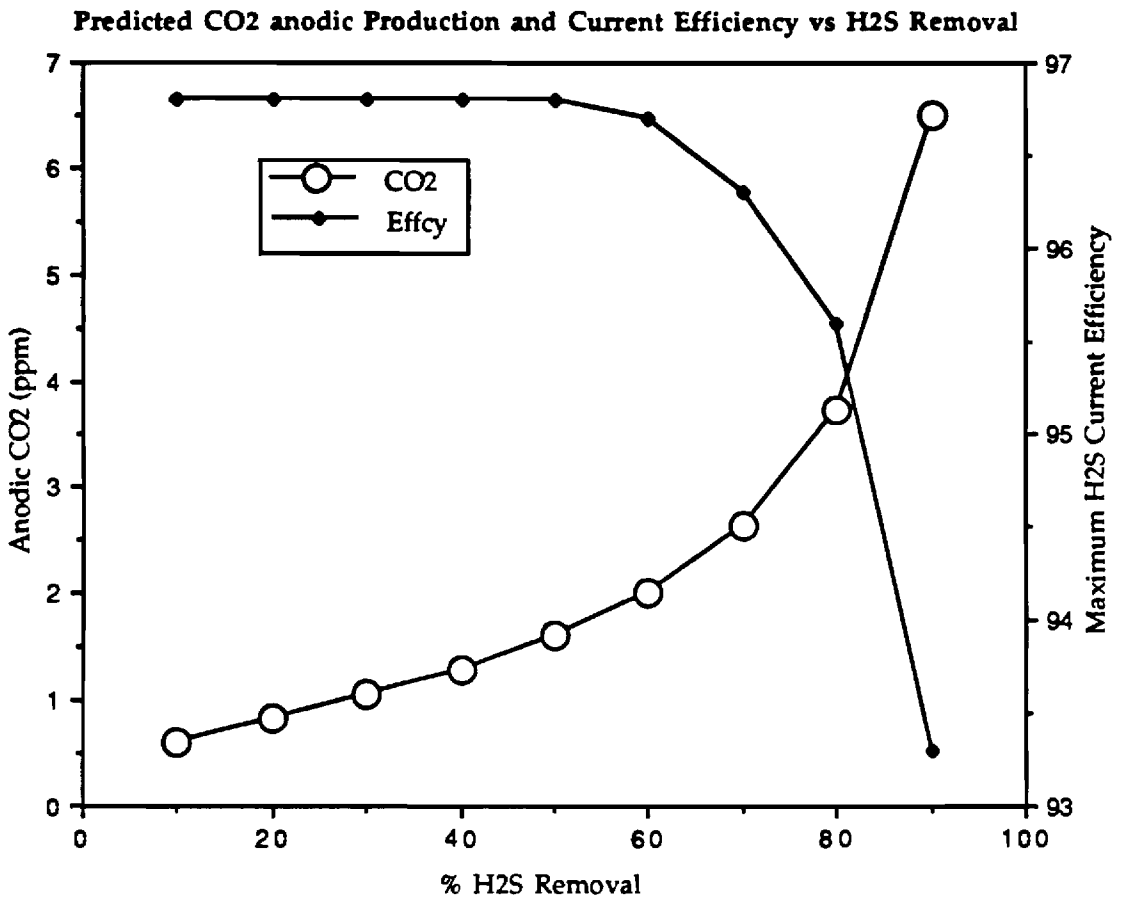


Figure 3. 100 ppm inlet H_2S

Examination of the cobalt-cathode electrochemical membrane separator (EMS), produced stoichiometric CO_2 removal and addition at both cathode and anode, respectively, before addition of H_2S. After introducing H_2S to the EMS, system gases equilibrated to 10% CO_2, 18% CO, 10% H_2O, 36% H_2, 26% N_2 and 90 ppmv H_2S after the water-gas shift reaction. H_2S removal at varying currents was attempted, starting with stoichiometric current (2 mA for a flow of 158 cc/min), and increasing to 200 mA. H_2S removal did not appear significant (< 10

ppmv), with continued stoichiometric CO_2 removal at the cathode and production at the anode. Further application of current in steps from 200 mA to 1.5 A revealed percentage of total H_2S removal coincided with percentage of total CO_2 removal, shown in Table IV. This trend was evidenced in past experiments with hydrogen cross-over present. Micro-cracks in the membrane that would enable hydrogen to cross from the process gas side (cathode side) to the sweep side (anode side) seem to be evident from Scanning Electron Microscopy (SEM) in pre-run analysis, Figure 8.

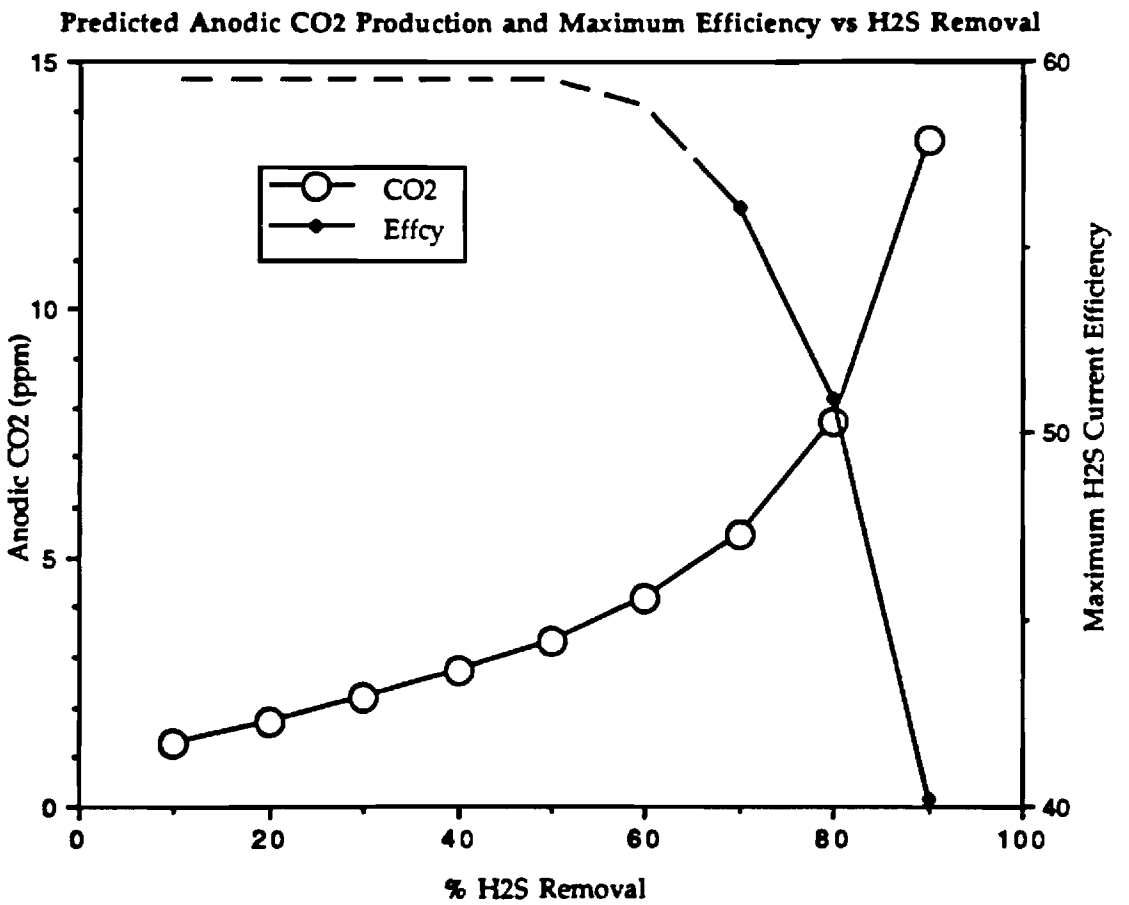


Figure 4. 10 ppm inlet H_2S

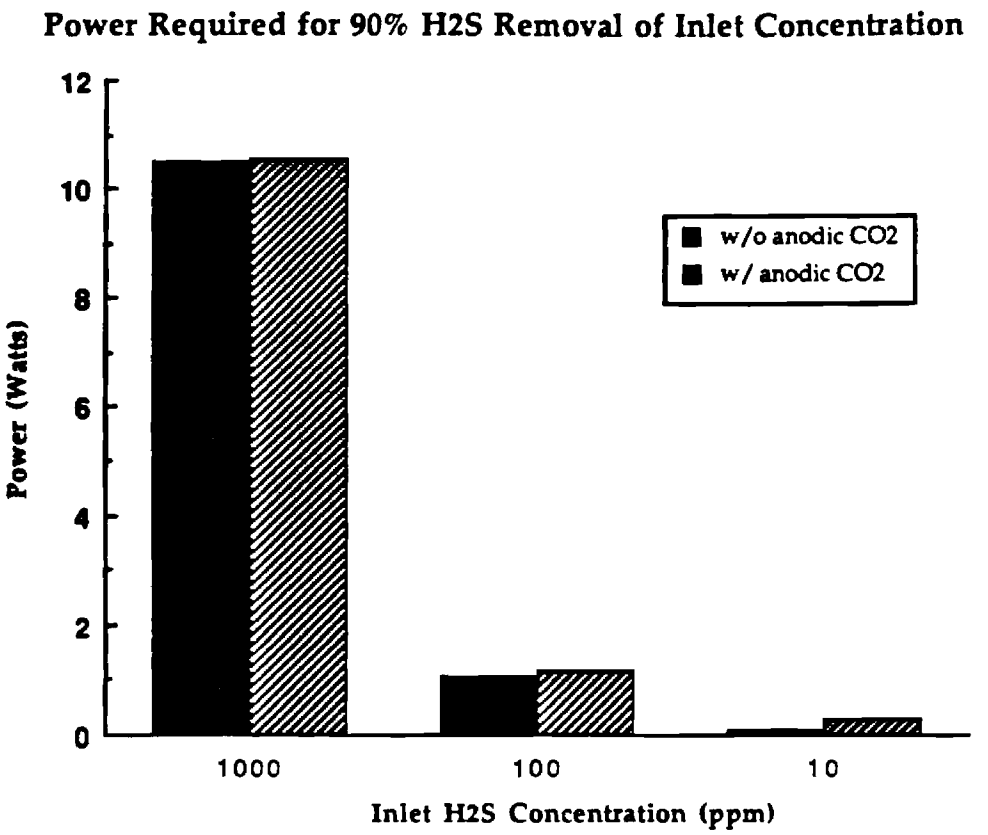


Figure 5. Power Estimates

Table IV. Percentage Removal with Applied Current

I_{app} (mA)	% of Total H_2S Removed	% of Total CO_2 Removed
200	0	10
500	28	30
1000	50	50
1500	70	75

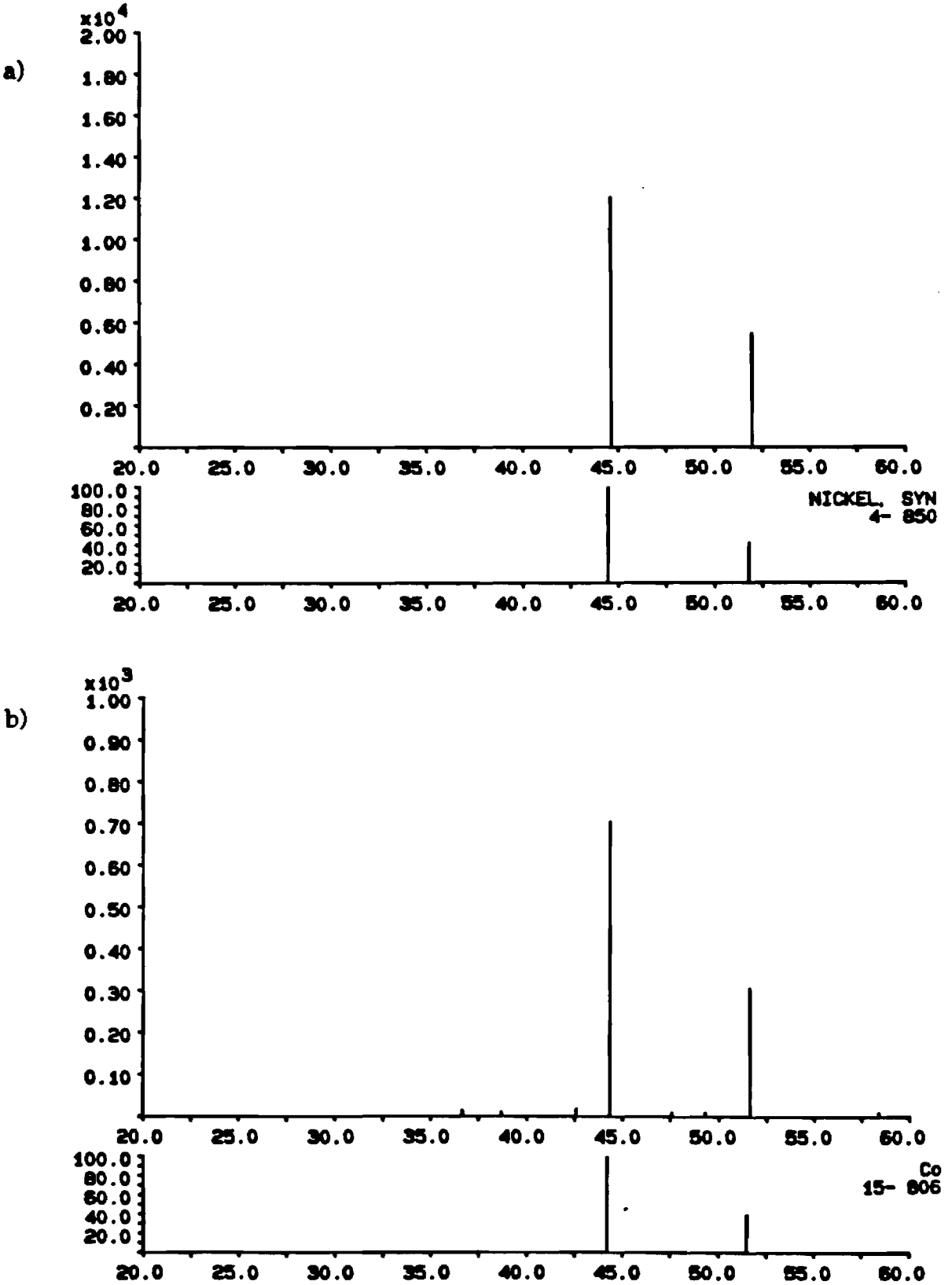
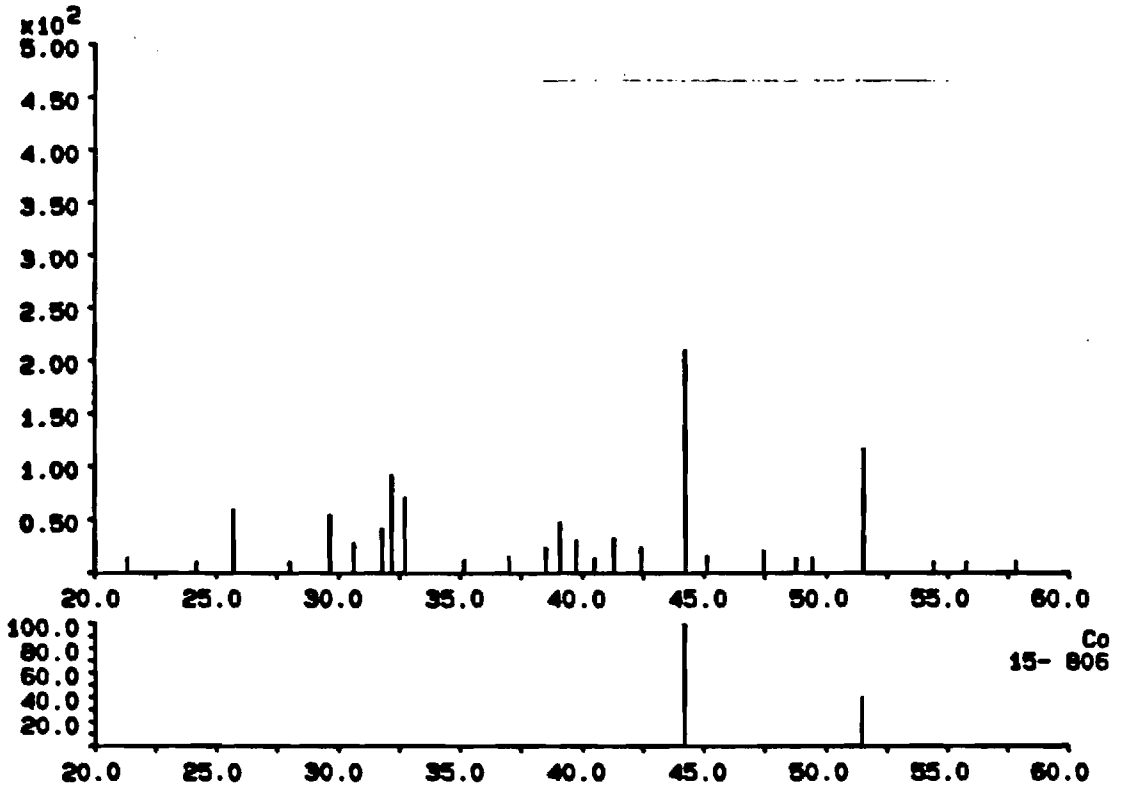


Figure 6. a) Pre-run Ni anode and b) Pre-run Co cathode

a)



b)

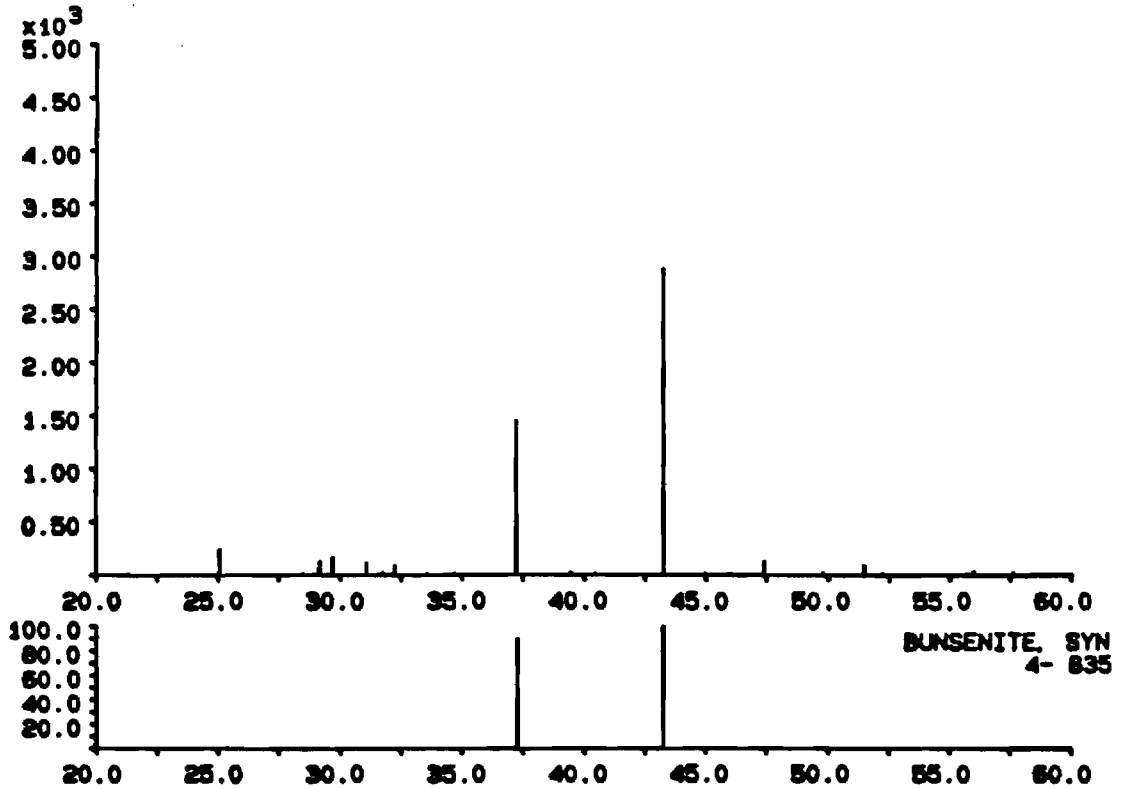


Figure 7. a.) Post-run Co cathode and b.) Post-run NiO anode

Figure 8. Scanning Electron Microscopic view of zirconia membrane.

If hydrogen cross-over occurs, two reactions are possible at the anode. One reaction is the oxidation of hydrogen and the sulfide ion to hydrogen sulfide.

$$H_2 + S^{2-} \rightarrow H_2S + 2e^-$$

Anode exit gases checked by gas chromatography showed no evidence of H_2S. The other possible reaction is the oxidation of hydrogen and carbonate to water and carbon dioxide.

$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$$

Gas chromatography did reveal minute amounts of water vapor on the anode side substantiating hydrogen cross-over. This creates loss of carbonate from the electrolyte, induces the favorability of carbonate reduction at the

cathode over H_2S due in part to the higher pressure of CO_2 and H_2O available at the cathode (order of 10^5 higher than H_2S) promoting the parasitic reaction.

Favored: $H_2S + 2e^- \rightarrow H_2 + S^{2-}$

Competing: $H_2O + CO_2 + 2e^- \rightarrow CO_3^{2-} + H_2$

Internal resistance remained ~1 ohm.

Ineffective removal due to hydrogen cross-over forced shut-down of the cell after 76 hours of operation. Post-mortem X-ray diffraction of electrode materials revealed a conversion of the Ni cathode to NiO (bunsenite), with the cathode remaining Co, Figure 7.

Summary

Initial results from the analytical model show favorable H_2S current efficiencies. Upper H_2S concentration removal resulted in a minuscule loss in current to the parasitic reaction (6) at 90% H_2S removal. Although the lower concentrations showed less efficiency, the amount of current needed for these removals are negligible.

The cobalt cathode used in the EMS proved stable and efficient. Removal of H_2S was deterred by the possibility of hydrogen cross-over from process gases creating alternate reactions unfavorable to the removal system. Application of back-pressure from the anode side of the cell was attempted to resolve H_2 cross-over, but proved ineffective. Examination of water vapor in the anode exit gases provided proof of the H_2 cross-over reactions parasitizing applied current.

Planned Work for Next Quarter

The main focus will be on H_2S current efficiency using a fabricated zirconia membrane with 100 ppmv H_2S fuel gas; hopefully, preventing alternate reactions due to hydrogen cross-over.

Work will continue with the analytical model; a complete economic analysis based on the completed model is the ultimate goal, if a match with real-time data exists.

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OMB Approval
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1. DOE Report No. 13

2. DOE Contract No. DE-PS22-91PC91282

3. Title High T Electrochemical Separation of H_2S from Coal Gasification Process Streams

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   - [ ] b. Conference paper:
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     - Date of conference _____
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8. Submitted by — Name and Position (Please print or type): Dr. Jack Winnick, Professor Dept. of Chemical Engineering

Organization: Georgia Tech

Signature: X [signature] JSR

Phone: (404) 894-2839

Date: 5/16/94

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9. Patent Clearance ("x" one)
   - [ ] a. DOE patent clearance has been granted by responsible DOE patent group.
   - [ ] b. Report has been sent to responsible DOE patent group for clearance.

Quarterly Progress Report:

High Temperature Electrochemical Separation Of H2S from Coal Gasification Process Streams

Grant DE-PS22-91PC91282

January 1, 1994 - March 31, 1994

by

Professor Jack Winnick

Georgia Institute of Technology

School of Chemical Engineering

Atlanta, GA 30332-0100

Objective

A method of polishing coal synthesis gas by an electrochemical membrane operation is being perfected. The operation takes advantage of an electrochemical potential gradient rather than conventional techniques, separating the H_2S from the coal gas stream, leaving only H_2 to enrich the exiting fuel gases. Sulfur is the by-product that is carried away by a separate inert sweep gas and condensed downstream. The technology is attractive due to simplicity as well as economics when compared to alternatives.

Experiments this quarter focused on removing 100 ppm inlet H_2S, utilizing laboratory fabricated cobalt cathodes.

Introduction

A schematic of the mechanism used for electrochemical separation is presented in Figure 1. The process gas, cleansed of particulates, passes over the cathode. Here the best Lewis acid, electron acceptor, will be reduced. In this case H_2S is favored, resulting in the following:

$$H_2S + 2e^- \rightarrow S^{2-} + H_2 \qquad (1)$$

The sulfide ions are transported, by migration and diffusion, across the membrane. Once the sulfide ion reaches the anode side, oxidation to elemental sulfur occurs by the following:

$$S^{2-} \rightarrow 1/2\ S_2 + 2e^- \qquad (2)$$

The vaporous sulfur is condensed downstream.

Processes to remove H_2S typically rely on low-to -ambient temperature adsorption, followed by sorbent regeneration and Claus plant treatment for conversion of H_2S to a salable by-product, sulfur. Although effective, this type of removal is very process-intensive as well as energy-inefficient due to low temperature operation. Gasification streams generally range from 500°C - 1000°C, requiring cooling before and reheating after process gas sweetening. Although these technologies have proven capable of meeting H_2S levels required by MCFC, there are several disadvantages inherent to these processes[1,2].

Alternative high temperature methods are presently available, but process drawbacks including morphological changes in catalytic beds[3] or inefficient molten salt sorbent processes[4] negate savings incurred through energy efficient removal temperatures.

An electrochemical membrane separation system for removing H_2S from coal gasification product streams is the subject of this investigation. The high operating temperature, flow-through design, and capability of selective H_2S removal and direct production of elemental sulfur offered by this process provide several advantages over existing and developmental H_2S removal technologies.

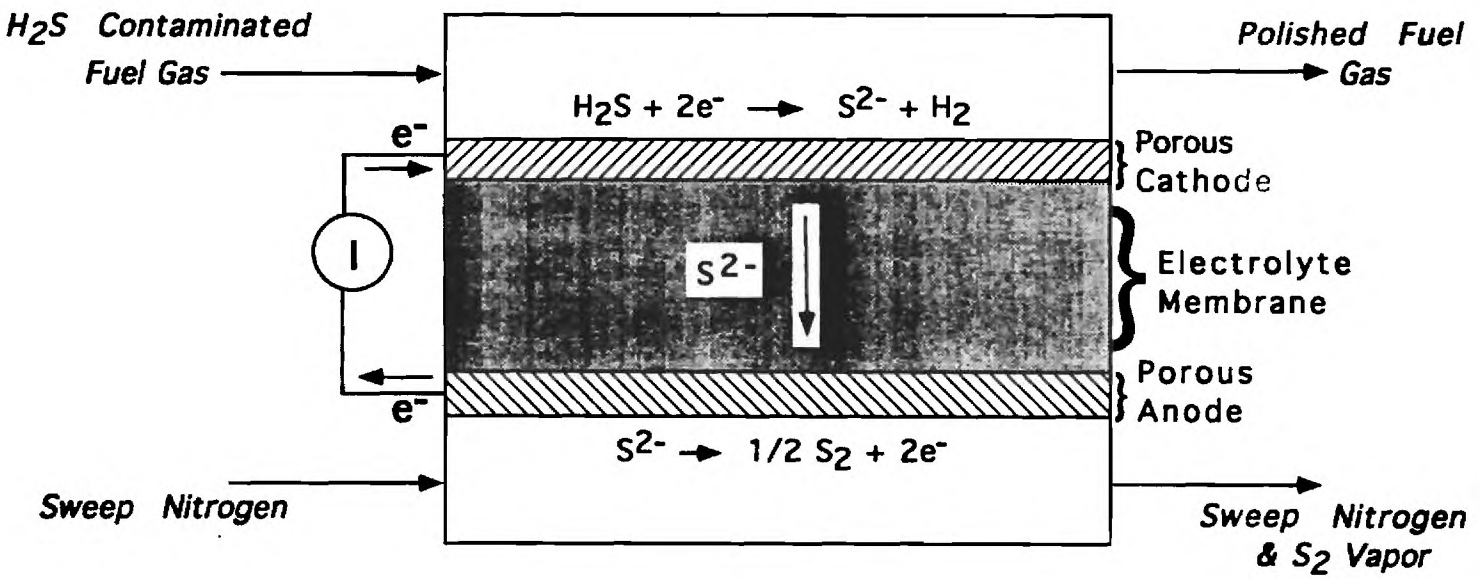

Figure 1. Conceptual Electrochemical Membrane Separator

Experimental Results

Two experiments (Run #17 & #18) examining the removal capability of the EMS with cobalt cathode were performed this quarter. The focus dealt with H_2S removal as well as impeding hydrogen cross-over from the process gas side (cathode) of the membrane to the sweep gas side (anode).

Gas cross-over Management

The cross-over of bulk process gases to the opposite electrode reduces cell performance. Current bench-scale membranes provide a complete barrier to bulk gas cross-over, although singular diffusion of hydrogen from the process gas remains a concern. An approach used by Molten Carbonate Fuel Cell (MCFC) technologist to reduce gas cross-over and reinforce the electrolyte matrix utilizes a *bubble pressure barrier* (bpb)[5,6], which consist of a mid-size pore region (relative to the membrane & electrode) between the membrane and the anode or cathode; a schematic representation is shown in Figure 2. If micro-cracks occur in the membrane from processing or thermal strains, the bpb provides an electrolyte-filled barrier to reinforce the membrane against gas cross-over. The bpb must have a uniform pore structure with intermediate pore size corresponding to existing membranes and electrodes to insure complete electrolyte entrainment; this provides a low resistance path for ion migration and diffusion as well as strong capillary forces to deter cross-over. A bubble barrier was incorporated into the EMS system for experiment #18 with minor success; increased amounts of electrolyte to infiltrate the bpb created a greater importance in retention to maintain an ionic pathway between electrodes.

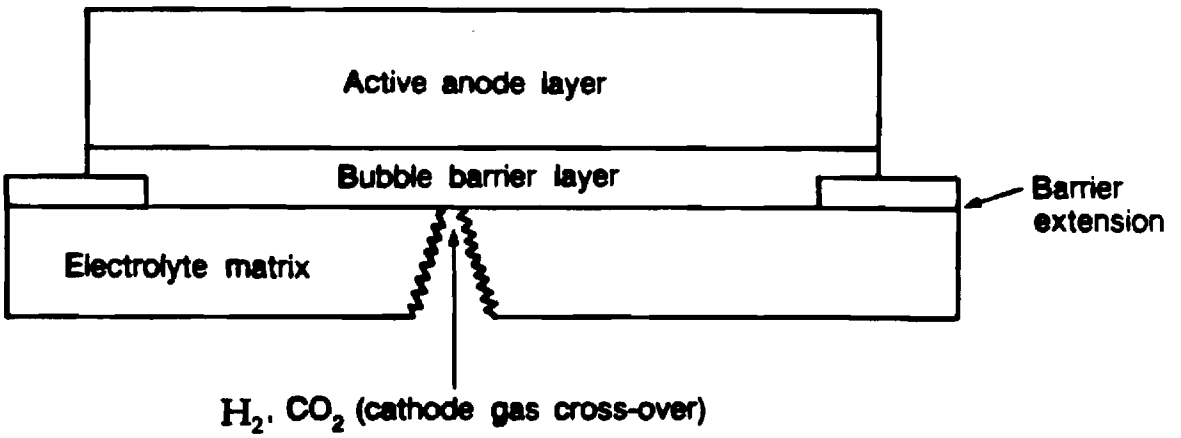

Figure 2. Bubble Barrier Set-up

Electrolyte Management

Loss of electrolyte is a consistent problem with the use of molten salt electrolytes; the mechanism of such losses is not well understood with electrolyte evaporation and alternate reactions involving system materials. Proposed mechanisms for the loss of electrolyte in the EMS are:

1) Material reactions upon process-gas seal formation:

$$2Al + 3/2\ O_2 \rightarrow Al_2O_3 \qquad K = 2.81 \times 10^{78}$$

$$Al_2O_3 + Li_2CO_3 \rightarrow 2LiAlO_2 + CO_2 \qquad K = 154$$

2) Evaporation at the anode due to a deficiency of CO_2:

$$Li_2CO_3 \rightarrow Li_2O + CO_2 \qquad K = 2.51 \times 10^{-5}$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \qquad K = 5.31 \times 10^{-15}$$

3) Evaporation into the surroundings:

$$2Li_2CO_3 + O_2 \rightarrow 2Li_2O_2 + 2CO_2 \qquad K = 3.88 \times 10^{-15}$$

$$2K_2CO_3 + O_2 \rightarrow 2K_2O_2 + 2CO_2 \qquad K = 7.37 \times 10^{-23}$$

with lithium carbonate, comprising 62 mole% electrolyte, being the least stable (larger K).

Quantitative evaporation studies were performed duplicating full-cell conditions. Three electrolyte filled crucibles placed in a controlled atmosphere furnace containing only nitrogen (similar to but less stringent than full-cell anode conditions) provided a large gradient for the evolution of CO_2; five days of testing released on average 1.6 grams of electrolyte. The crucibles were then placed in a conventional oven to duplicate evaporation by mechanism (3); 24 hours of exposure evolved on average 30 grams of electrolyte leaving a crystalline residue of Li_2O_2 & Li_2O by:

$$Li_2O_2 \rightarrow Li_2O + 1/2\ O_2 \qquad \Delta G = -41.54\ KJ/mol \qquad K = 225$$

Absolute verification of Li_2O by X-ray diffraction could not be accomplished due to sample contamination, but future membrane analysis by x-ray should provide

conclusive evidence of Li_2O formation; Li_2O_2 is not in the x-ray diffraction software package so uncertainity exist in verification of this molecule.

Run#17

Cell materials consisted of a cobalt cathode (80% porous), Ni anode (85% porous), a fabricated zirconia membrane (69% porous), housings of MACOR (machineable ceramic), aluminum foil gasket seals, and a prepressed disk of $(Li/K)_2CO_3$ (5 grams) corresponding to the void volume in the zirconia membrane. Electrode materials were verified by x-ray diffraction.

Initial examination of the cobalt-cathode electrochemical membrane separator (EMS), produced stoichiometric transport of CO_3^{2-}; however, material problems (i.e. cracking of ceramic housings and loss of flow-tube seals), prompted immediate shut-down after 24 hours of operation.

Run#18

Cell materials consisted of a cobalt cathode (80% porous), Ni-mesh anode (95% porous), a fabricated zirconia membrane (69% porous) coupled with a bpb (purchased zirconia membrane (66% porous)), housings of MACOR (machineable ceramic), aluminum foil gasket seals, and a prepressed disk of $(Li/K)_2CO_3$ (14 grams) corresponding to the void volume in the two zirconia matrices. Electrode materials were verified by x-ray diffraction.

Problems arose early in the start-up process after the electrolyte converted to the molten state. Consistent addition of electrolyte provided only temporary solutions to the problem of high cross-cell resistance from loss of electrolyte. A consistent ionic pathway between electrodes was never established negating efforts to transport carbonate; therefore, H_2S was never introduced into the cell. Shut-down occurred after 168 hours.

Summary

The cobalt cathode used in the EMS proved stable and efficient. Removal of H_2S was deterred by extensive electrolyte loss discussed earlier. Mechanism 1 is the least imposing upon complete conversion of Al to $LiAlO_2$ (time ~ 200 hrs). Mechanism 2 representing full-cell anode conditions exhibited minor evaporation by natural convection of electrolyte in crucible tests, but should increase considerably in real-time experiments due to the convective flow of N_2 over the anode pores. The solution of CO_2 evolution at the anode involves a mixture of CO_2 & N_2 (CO_2 = cathodic concentration) reducing the driving force for electrolyte loss. Mechanism 3 creates the greatest problem due atmospheric evaporation. Reducing the surface area exposed to the atmosphere is the only solution, a method of which is still under development.

Planned Work for Next Quarter

The main focus will be on H_2S current efficiency using a fabricated zirconia membrane and bubble barrier with 100 ppmv H_2S fuel gas; hopefully, preventing alternate reactions due to hydrogen cross-over. Implementation of CO_2 with the anode gas should alleviate anodic electrolyte evaporation.

References

1. U.S. Dept. of Energy, Fuel Cell: A Handbook, DOE/METC-88/6090, Morgantown, West Virginia, 1988.
1. EPRIEM-1333, *Assessment of Sulfur Removal Processes for Advanced Fuel Cell Systems, Final Report*, C.F. Braun and Co., Alhambra, CA, Jan., 1980.
2. Vidt, E.J., DOE/METC DE-AC-21-81MC16220, DE82013942, Westinghouse, Dec., 1981.
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4. Lyke, S.E., DOE/MC/19077-1803, DE8500961, Battelle Pacific Northwestern Laboratories, Jan. 1985.

5. U.S. Dept. of Energy, Fuel Cell: A Handbook, DOE/METC-88/6090, Morgantown, West Virginia, 1988.

6. U.S. Dept. of Energy, Fuel Cells: Technology Status Report, DOE/METC-92/0276, Morgantown, West Virginia, 1992.

DOE F 1332.16 (10-84)
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8. Submitted by Dr. Jack Winnick
   Name and Position (Please print or type) Professor Dept. of Chemical Engineering
   Organization Georgia Tech
   Signature
   Phone (404) 894-2839
   Date 8/18/94

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Quarterly Progress Report:

High Temperature Electrochemical Separation Of H2S from Coal Gasification Process Streams

Grant DE-PS22-91PC91282

April 1, 1994 - June 30, 1994

by

Professor Jack Winnick

Georgia Institute of Technology

School of Chemical Engineering

Atlanta, GA 30332-0100

Objective

A method of polishing coal synthesis gas by an electrochemical membrane operation is being perfected. The operation takes advantage of an electrochemical potential gradient rather than conventional techniques, separating the H_2S from the coal gas stream, leaving only H_2 to enrich the exiting fuel gases. Sulfur is the by-product that is carried away by a separate inert sweep gas and condensed downstream. The technology is attractive due to simplicity as well as economics when compared to alternatives.

Experiments this quarter focused on removing 100 ppm inlet H_2S, utilizing laboratory fabricated cobalt cathodes. Microscopic analysis of membrane morphology was also investigated to determine if any high temperature restructuring occurs.

Introduction

A schematic of the mechanism used for electrochemical separation is presented in Figure 1. The process gas, cleansed of particulates, passes over the cathode. Here the best electron acceptor will be reduced. In this case H_2S is favored, resulting in the following:

$$H_2S + 2e^- \rightarrow S^{2-} + H_2 \qquad (1)$$

The sulfide ions are transported, by migration and diffusion, across the membrane. Once the sulfide ion reaches the anode side, oxidation to elemental sulfur occurs by the following:

$$S^{2-} \rightarrow 1/2\ S_2 + 2e^- \qquad (2)$$

The vaporous sulfur is condensed downstream.

Processes to remove H_2S typically rely on low-to -ambient temperature adsorption, followed by sorbent regeneration and Claus plant treatment for conversion of H_2S to a salable by-product, sulfur. Although effective, this type of removal is very process-intensive as well as energy-inefficient due to low temperature operation. Gasification streams generally range from 500°C - 1000°C, requiring cooling before and reheating after process gas sweetening. Although these technologies have proven capable of meeting H_2S levels required by MCFC, there are several disadvantages inherent to these processes[1,2].

Alternative high temperature methods are presently available, but process drawbacks including morphological changes in catalytic beds[3] or inefficient

molten salt sorbent processes[4] negate savings incurred through energy efficient removal temperatures.

An electrochemical membrane separation system for removing H_2S from coal gasification product streams is the subject of this investigation. The high operating temperature, flow-through design, and capability of selective H_2S removal and direct production of elemental sulfur offered by this process provide several advantages over existing and developmental H_2S removal technologies.

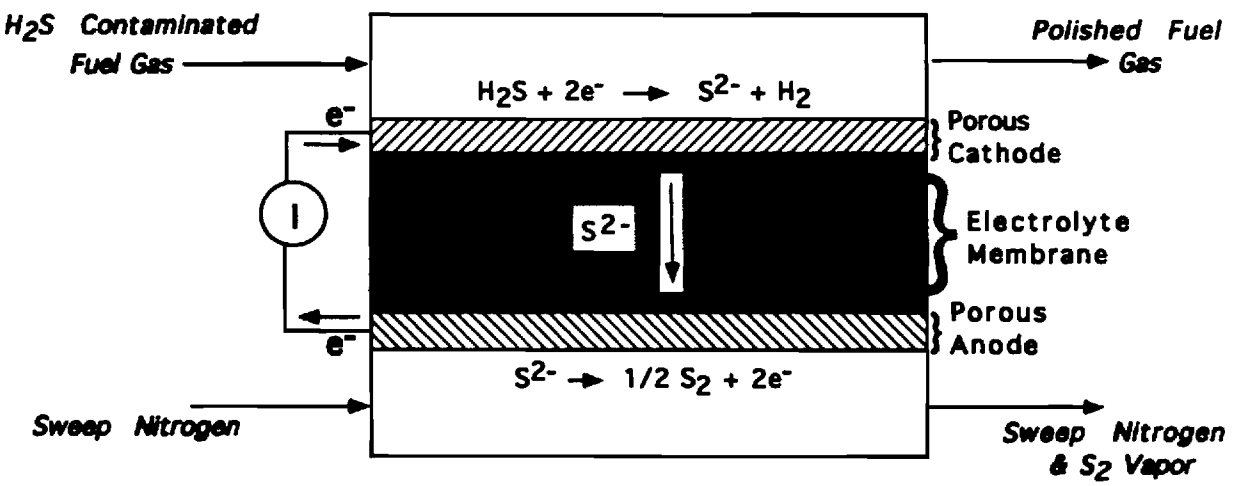

Figure 1. Conceptual Electrochemical Membrane Separator

Experimental Results

An experiment (Run #19) examining the removal capability of the EMS with cobalt cathode was performed this quarter. The focus dealt with H_2S removal as well as impeding hydrogen cross-over from the process gas side (cathode) of the membrane to the sweep gas side (anode). Secondary concerns involved electrolyte evaporation into the surroundings and gas seals to retain process-gases.

Gas cross-over Management

The cross-over of bulk process gases to the opposite electrode reduces cell performance. Current bench-scale membranes provide a complete barrier to bulk gas cross-over, although singular diffusion of hydrogen from the process gas remains a concern. An approach used by Molten Carbonate Fuel Cell (MCFC) technologist to reduce gas cross-over and reinforce the electrolyte matrix utilizes a *bubble pressure barrier* (bpb)[5,6], which consist of a mid-size pore region (relative to the membrane & electrode) between the membrane and the anode or cathode. If micro-cracks occur in the membrane from processing or thermal strains, the bpb provides an electrolyte-filled barrier to reinforce the membrane against gas cross-over. The bpb must have a uniform pore structure with intermediate pore size corresponding to existing membranes and electrodes to insure complete electrolyte entrainment; this provides a low resistance path for ion migration and diffusion as well as strong capillary forces to deter cross-over. A bubble barrier incorporated into the EMS system showed minor success[7]; however, increased amounts of electrolyte required to infiltrate the bpb creates a greater importance in electrolyte retention to maintain ionic mobility between electrodes.

Electrolyte Management

Loss of electrolyte is a consistent problem with the use of molten salt electrolytes; the mechanism of such losses is not well understood with electrolyte evaporation and alternate reactions involving system materials. Proposed mechanisms for the loss of electrolyte in the EMS are:

1) Material reactions upon process-gas seal formation:

$$2Al + 3/2\ O_2 \rightarrow Al_2O_3 \qquad K = 2.81 \times 10^{78}$$

$$Al_2O_3 + Li_2CO_3 \rightarrow 2LiAlO_2 + CO_2 \qquad K = 154$$

2) Evaporation at the anode due to a deficiency of CO_2:

$$Li_2CO_3 \rightarrow Li_2O + CO_2 \qquad K = 2.51 \times 10^{-5}$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \qquad K = 5.31 \times 10^{-15}$$

3) Evaporation into the surroundings:

$$2Li_2CO_3 + O_2 \rightarrow 2Li_2O_2 + 2CO_2 \qquad K = 3.88 \times 10^{-15}$$

$$2K_2CO_3 + O_2 \rightarrow 2K_2O_2 + 2CO_2 \qquad K = 7.37 \times 10^{-23}$$

with lithium carbonate, comprising 62 mole% electrolyte, being the least stable (larger K).

Quantitative evaporation studies were performed duplicating full-cell conditions[7]. Mechanism (2) & (3) were investigated with evaporation by mechanism (3) entailing the predominant amount of electrolytic losses; 24 hours of exposure evolved on average 30 grams of electrolyte leaving a crystalline residue of Li_2O_2 & Li_2O by:

$$Li_2O_2 \rightarrow Li_2O + 1/2\ O_2 \qquad \Delta G = -41.54\ KJ/mol \qquad K = 225$$

<u>*Run#19*</u>

Cell materials consisted of a cobalt cathode (80% porous), Ni-mesh anode (95% porous) purchased from MEMTEC, a fabricated zirconia membrane (69% porous), housings of MACOR (machineable ceramic), aluminum foil gasket seals,

and a prepressed disk of $(Li/K)_2CO_3$ (10 grams) corresponding to the void volume in the zirconia matrices. Electrode materials were verified by x-ray diffraction and Scanning Electron Microscopy (S.E.M), illustrated in Figure 2.

Problems arose early in the start-up process after the electrolytic powder converted to the molten state. Consistent addition of electrolyte provided only temporary solutions to the problem of high cross-cell resistance from loss of electrolyte. A consistent ionic pathway between electrodes was never established negating efforts to transport carbonate; therefore, H_2S was never introduced into the cell. Shut-down occurred after 72 hours.

a) b)

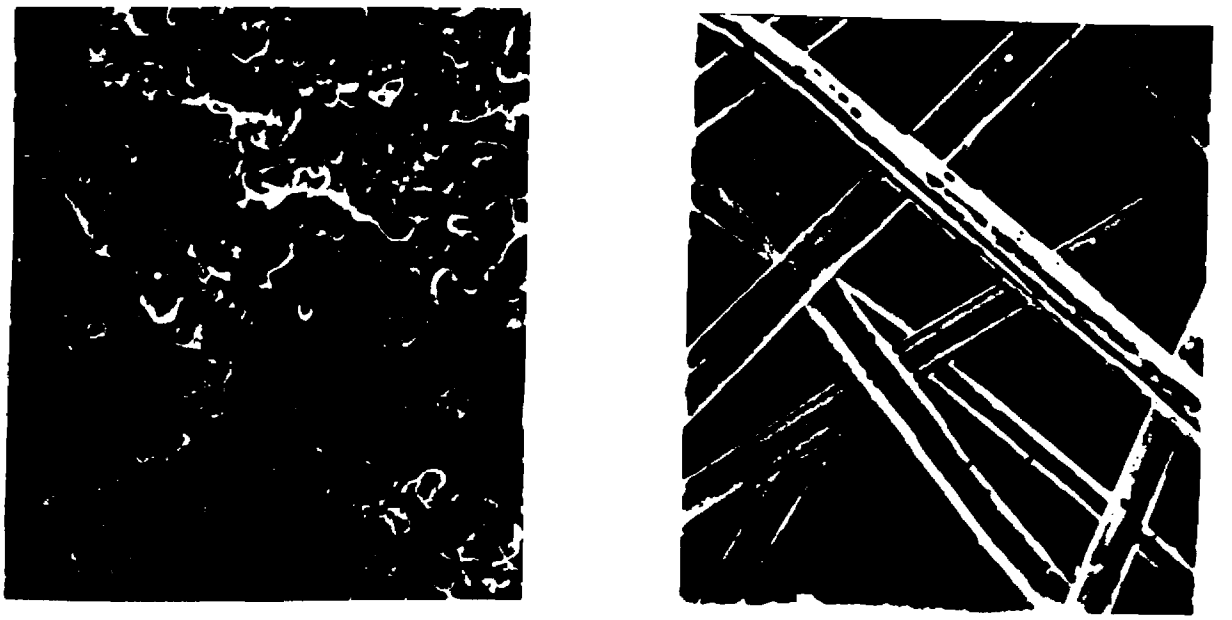

Figure 2. Electrode materials a) Co cathode, and b) Ni mesh anode.

Membrane Analysis

Analysis of zirconia materials purchased from Zircar and incorporated into the Electrochemical Membrane Separator (E.M.S.) provided additional information to improve the consistency of the process. All analysis was done utilizing X-ray diffraction to determine crystal orientation fluctuations in the basic structure upon thermal cycling. Severe complications from materials failure due to thermal restructuring could effect system efficiencies, therefore removal performance of the E.M.S.. Testing was completed on numerous samples manufactured differently but with identical chemical make-up; all samples were heated above E.M.S. system temperatures (650 ^{o}C) for approximately 50 hours. X-ray diffraction before and after thermal cycling was then compared to identify morphological conditions.

Zirconia is used in the stabilized form as a high temperature material in several electrochemical applications due to the stability of the crystal lattice. Several dopants can stabilize zirconia depending on the mole percentage; yttria used by Zircar as a stabilizer, must be present between ~6-56 mole % to maintain the stable cubic form necessary for high temperature operation. Current zirconia products purchased as membrane materials contained ~ 4.5 - 5.7 mole % yttria; thus according to the zirconia-yttria phase diagram, Figure 3, an admixture of cubic zirconia with the unstable monoclinic zirconia exist; the amount of cubic zirconia increasing with mole percent yttria.

X-ray diffraction data on Zircar products ($Y_{0.045}Zr_{0.955}O_{1.97}$) gave a similar fingerprint to the yttria-doped zirconia contained in the software ($Y_{0.15}Zr_{0.85}O_{1.925}$), Figure 4; however, this is not a confirmation of the materials stability due to the inability to acquire a standard containing 4.5 mole % yttria-doped zirconia. Further tests must be done.

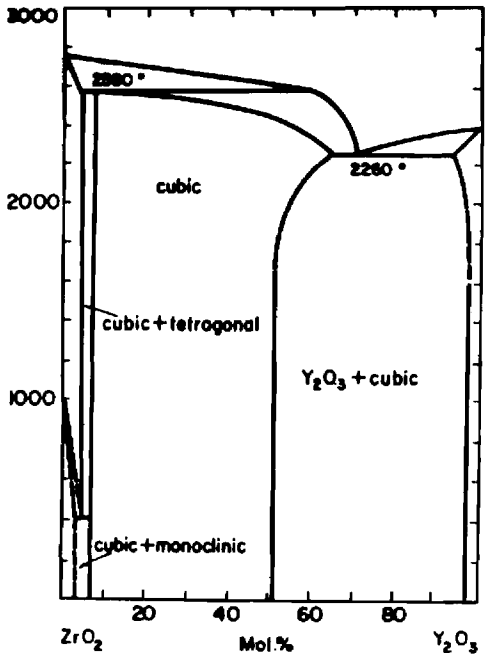

FIG. 354.—System Y_2O_3–ZrO_2.

H. E. Otto, private communication Dec. 27, 1961. See also, P. S. Duwez, F. H. Brown, Jr., and F. Odell, *J. Electrochem. Soc.*, 98, 360 (1951).

Figure 3. Zirconia-Yttria phase diagram

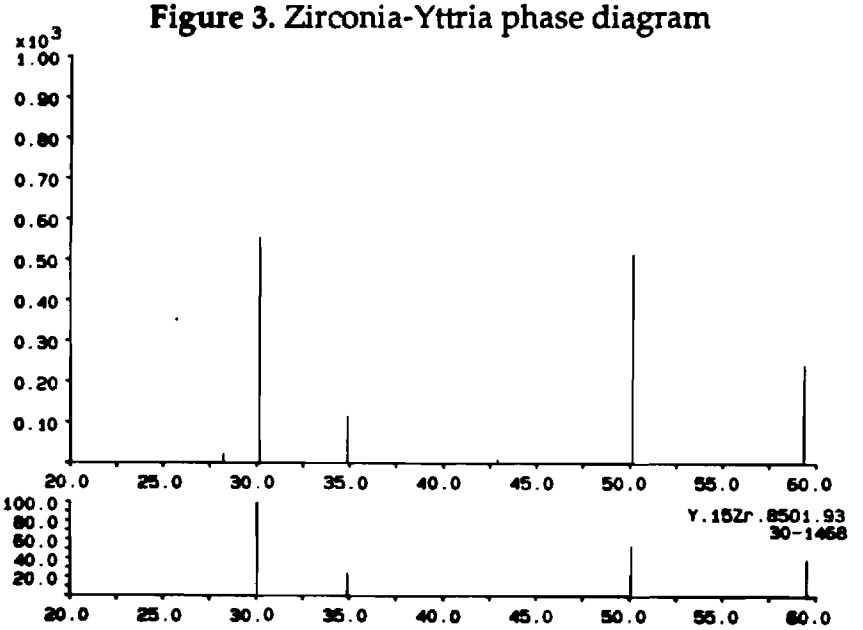

Figure 4. X-ray diffraction comparison of Zircar material ($Y_{0.045}Zr_{0.955}O_{1.97}$) to database material ($Y_{0.15}Zr_{0.85}O_{1.925}$).

Summary

The cobalt cathode used in the EMS proved stable and efficient. Removal of H_2S was deterred by extensive electrolyte loss discussed earlier. Mechanism 1 is the least imposing upon complete conversion of Al to $LiAlO_2$. Mechanism 2

representing full-cell anode conditions exhibited minor evaporation by natural convection of electrolyte in crucible tests, but should increase considerably in real-time experiments due to the convective flow of N_2 over the anode pores. The solution of CO_2 evolution at the anode involves a mixture of CO_2 & N_2 (CO_2 = cathodic concentration) reducing the driving force for electrolyte loss. Mechanism 3 creates the greatest problem due to atmospheric evaporation. Reducing the surface area exposed to the atmosphere and utilization of a controlled atmosphere furnace containing CO_2 and a block of graphite to consume any excess oxygen are proposed solutions.

Planned Work for Next Quarter

The main focus will be on H_2S current efficiency using a fabricated zirconia membrane with 100 ppmv H_2S fuel gas; hopefully, preventing alternate reactions due to hydrogen cross-over. Implementation of CO_2 with the anode gas should alleviate anodic electrolyte evaporation, along with implementation of the CO_2 atmospheric furnace.

References

1. U.S. Dept. of Energy, Fuel Cell: A Handbook, DOE/METC-88/6090, Morgantown, West Virginia, 1988.
1. EPRIEM-1333, *Assessment of Sulfur Removal Processes for Advanced Fuel Cell Systems, Final Report*, C.F. Braun and Co., Alhambra, CA, Jan., 1980.
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6. U.S. Dept. of Energy, Fuel Cells: Technology Status Report, DOE/METC-92/0276, Morgantown, West Virginia, 1992.

7. Winnick, J., Quarterly Progress Report #13, DOE grant DE-FG-91PC91288.

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3. Title High Temperature Electrochemical Separation of H_2S from Coal Gasification Process Streams

4. Type of Document ("x" one)
   - [x] a. Scientific and technical report
   - [ ] b. Conference paper:
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   Name and Position (Please print or type): Professor Dept. of Chemical Engineering
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Experimental analysis was not possible this quarter due to a change of laboratories. This change makes possible improved experimental conditions. Predominant work dealt with improving the current process, improving the oven structure to accommodate a controlled atmosphere heating, regulating oven conditions using resistance control, etc..

Introduction

A schematic of the mechanism used for electrochemical separation is presented in Figure 1. The process gas, cleansed of particulates, passes over the cathode. Here the best electron acceptor will be reduced. In this case H_2S is favored, resulting in the following:

$$H_2S + 2e^- \rightarrow S^{2-} + H_2 \qquad (1)$$

The sulfide ions are transported, by migration and diffusion, across the membrane. Once the sulfide ion reaches the anode side, oxidation to elemental sulfur occurs by the following:

$$S^{2-} \rightarrow 1/2\ S_2 + 2e^- \qquad (2)$$

The vaporous sulfur is condensed downstream.

Processes to remove H_2S typically rely on low-to -ambient temperature adsorption, followed by sorbent regeneration and Claus plant treatment for conversion of H_2S to a salable by-product, sulfur. Although effective, this type of removal is very process-intensive as well as energy-inefficient due to low temperature operation. Gasification streams generally range from 500°C - 1000°C, requiring cooling before and reheating after process gas sweetening. Although these technologies have proven capable of meeting H_2S levels required by MCFC, there are several disadvantages inherent to these processes[1,2].

Alternative high temperature methods are presently available, but process drawbacks including morphological changes in catalytic beds[3] or inefficient molten salt sorbent processes[4] negate savings incurred through energy efficient removal temperatures.

An electrochemical membrane separation system for removing H_2S from coal gasification product streams is the subject of this investigation. The high operating temperature, flow-through design, and capability of selective H_2S removal and direct production of elemental sulfur offered by this process provide several advantages over existing and developmental H_2S removal technologies.

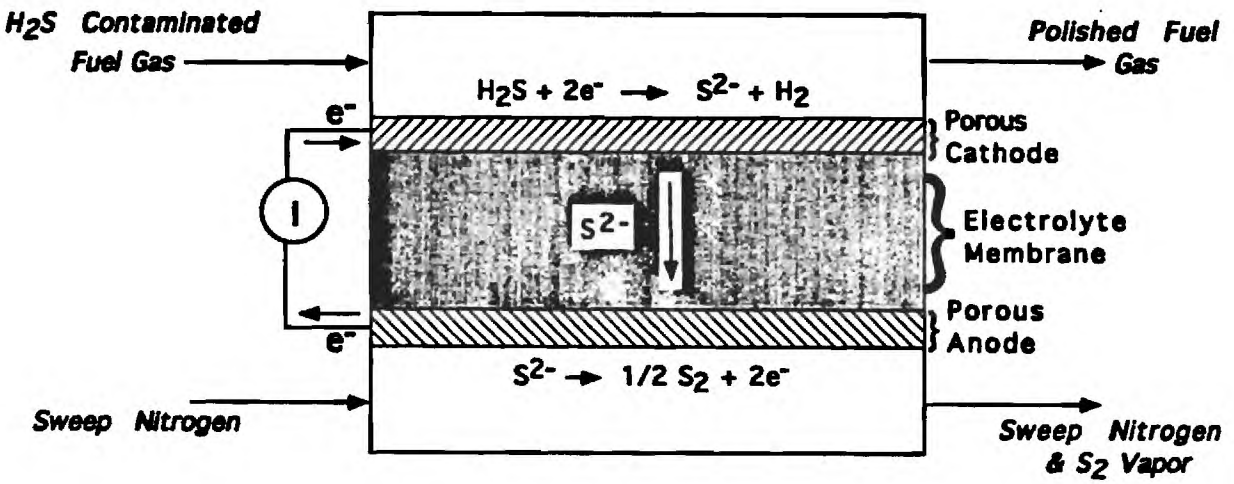


Figure 1. Conceptual Electrochemical Membrane Separator

<u>Laboratory Improvement</u>

The impetus for controlling the atmosphere around the Electrochemical Membrane Separator relates to electrolyte from the process membrane. In a CO_2 environ the partial pressure of CO_2 should push the equilibrium for certain unfavorable reactions to the left. Abatement of CO_2 evolution is at present a focal point to extended life and efficient removal utilizing the E.M.S. system.

Electrolyte Management

Loss of electrolyte is a consistent problem with the use of molten salt electrolytes; the mechanism of such losses is not well understood with electrolyte evaporation and alternate reactions involving system materials. Proposed mechanisms for the loss of electrolyte in the EMS are:

1) Material reactions upon process-gas seal formation:

$$2Al + 3/2\ O_2 \rightarrow Al_2O_3 \qquad K = 2.81 \times 10^{78}$$

$$Al_2O_3 + Li_2CO_3 \rightarrow 2LiAlO_2 + CO_2 \qquad K = 154$$

2) Evaporation at the anode due to a deficiency of CO_2:

$$Li_2CO_3 \rightarrow Li_2O + CO_2 \qquad K = 2.51 \times 10^{-5}$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \qquad K = 5.31 \times 10^{-15}$$

3) Evaporation into the surroundings:

$$2Li_2CO_3 + O_2 \rightarrow 2Li_2O_2 + 2CO_2 \qquad K = 3.88 \times 10^{-15}$$

$$2K_2CO_3 + O_2 \rightarrow 2K_2O_2 + 2CO_2 \qquad K = 7.37 \times 10^{-23}$$

with lithium carbonate, comprising 62 mole% electrolyte, being the least stable (larger K).

Quantitative evaporation studies were performed duplicating full-cell conditions[7]. Mechanism (2) & (3) were investigated with evaporation by mechanism (3) entailing the predominant amount of electrolytic losses; 24 hours of exposure evolved on average 30 grams of electrolyte leaving a crystalline residue of Li_2O_2 & Li_2O by:

$$Li_2O_2 \rightarrow Li_2O + 1/2\ O_2 \qquad \Delta G = -41.54\ KJ/mol \qquad K = 225$$

Matrices Analysis

Zirconia textiles are used in a number of high temperature electrochemical applications (e.g. electrode separators, diaphragms, etc.) due to their high temperature stability (yttria-stabilized zirconia is stable up to 2600 ^{o}C) and corrosion resistance to molten salts and metals(e.g. aluminum, copper, and nickel based alloys)[8]. Successful utilization of zirconia membranes for electrolyte entrainment in the Electrochemical Membrane Separator(E.M.S.) has been proven in real-time experiments[9]. Use of yttria-stabilized zirconia in the E.M.S. system was based on the electrochemical and thermal properties of the cloth (thin, open-

pore structure, strength, electrically insulating, high temperature resistant, good wettability, and *bubble pressure resistance*)[8]. Identifying possible structural changes in the membrane material as a function of temperature was investigated to insure operating stability in the E.M.S..

Stabilization of zirconia by doping yttria occurs at ~ 6 mol%/10.5 wt% yttria[10]; the resulting crystal orientation is the cubic crystal lattice. Cubic stabilized zirconia has the fluorite structure with O^{2-} ions arranged in the simple cubic form and half the interstitial space occupied by Zr^{4+}; substitution of lower valence cations (e.g. Y^{3+}) creates O^{2-} vacancies[11]. Half of the yttria-doped zirconia unit cell is shown in Figure 2.

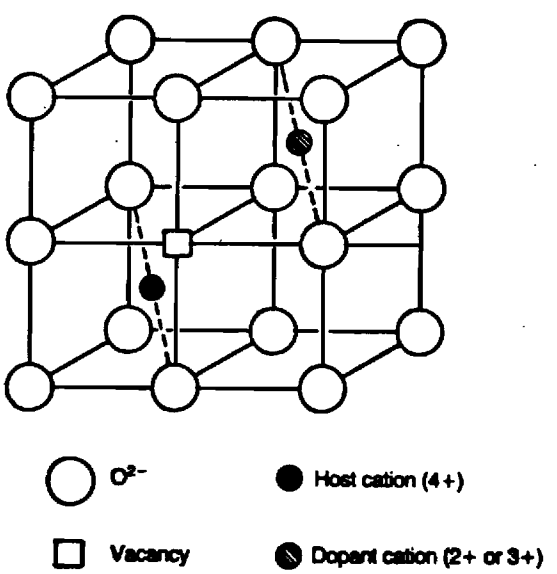


Figure 2. Cubic structure of yttria-stabilized zirconia.

The doping concentration strongly effects the structural behavior of zirconia upon thermal cycling; three main crystal structures are apparent with varying

yttria concentration (monoclinic, tetragonal, and cubic) shown in Figure 3. The zirconia-yttria phase diagram is shown in Figure 4. The monoclinic phase exist with yttria concentrations up to 3 mol%.

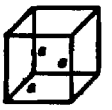
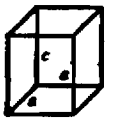
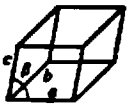
System	Axial Lengths and Angles*	Unit Cell Geometry
Cubic	$a = b = c,\ \alpha = \beta = \gamma = 90°$	
Tetragonal	$a = b \neq c,\ \alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c,\ \alpha = \gamma = 90° \neq \beta$	

Figure 3. Three prevalent crystal structure of yttria-doped zirconia.

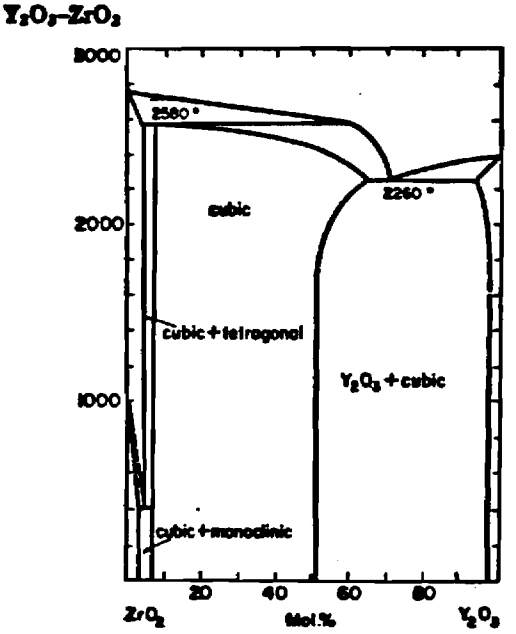


FIG. 354.—System Y_2O_3–ZrO_2.

H. E. Otto, private communication Dec. 27, 1961. See also, P. S. Duwez, F. H. Brown, Jr., and F. Odell, *J. Electrochem. Soc.*, 98, 360 (1951).

Figure 4. Phase diagram of the yttria-zirconia system.

Yttria concentrations between 4 and 5 mol% create an admixture of cubic and monoclinic zirconia; the amount of cubic zirconia increasing with dopant concentration. For a yttria content of ~ 7 to 55 mol% the stabilized cubic form is present, thermally stable up to ~2000 °C. Problems arise with admixtures of cubic and monoclinic or tetragonal species which are present at lower yttria concentrations (1 - 5 mol%); conversion of the monoclinic phase to the tetragonal phase is dependent on temperature and concentration and accompanied by a large volume change, shown in Figure 5. This volume change

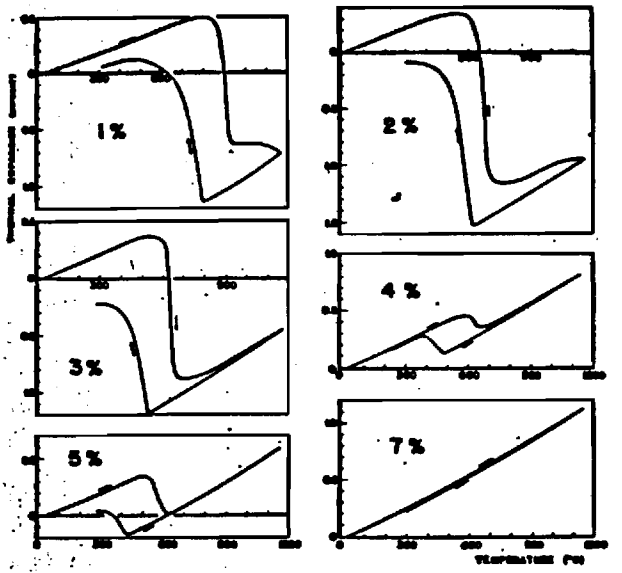


Figure 5[10]. Per cent volume change of yttria-doped zirconia upon conversion of monoclinic to tetragonal back to monoclinic vs. temperature, at varying dopant concentrations.

signifies the importance of producing/purchasing a matrix material capable of structural stability at E.M.S. system temperatures (~ 650 °C). Since fully cubic zirconia (therefore structural stable) occurs with dopant concentration of ~ 6 - 55 mol%, yttria content is a major factor in purchasing/producing a matrix material

of zirconia to maintain a consistent equilibrium within the E.M.S. system (e.g. provide a consistent pathway for ion mobility, maintain intimate contact between membrane and electrodes, sustain process-gas seals, etc.).

Since Zircar stabilizes their zirconia materials with 8 - 10 wt% / 4.5 - 5.7 mol% dopant (yttria) and previous experimentation[10] revealed ~ 6 mol% dopant (yttria) is required to completely stabilize zirconia, crystallographic analysis was performed by X-ray diffraction to ensure the stability of yttria-doped zirconia purchased/produced by Zircar for use in the E.M.S. system. Three membranes were tested each manufactured differently with identical chemical make-up. X-ray diffraction was performed on the three samples, before and after thermal cycling above E.M.S temperatures. In all cases (before and after thermal treatment) the structural comparisons to the x-ray diffraction database of materials were favorable with patterns shown in figure 6. Exact comparisons of Zircar's material ($Y_{0.045}Zr_{0.954}O_{1.9755}$) to the database structure ($Y_{0.15}Zr_{0.85}O_{1.925}$) creates some uncertainty since 15 mol% yttria-doped zirconia is well within the stabilized cubic range and 4.5 mol% yttria-doped zirconia is slightly below the stabilized range (containing an admixture of monoclinic and cubic) shown in Figure 4.

Summary

Mechanism 1 is the least imposing upon complete conversion of Al to $LiAlO_2$. Mechanism 2 representing full-cell anode conditions exhibited minor evaporation by natural convection of electrolyte in crucible tests, but should increase considerably in real-time experiments due to the convective flow of N_2 over the anode pores. The solution of CO_2 evolution at the anode involves a mixture of CO_2 & N_2 (CO_2 = cathodic concentration) reducing the driving force for electrolyte loss. Mechanism 3 creates the greatest problem due to

atmospheric evaporation. Reducing the surface area exposed to the atmosphere and utilization of a controlled atmosphere furnace containing CO_2 and a block of graphite to consume any excess oxygen are proposed solutions.

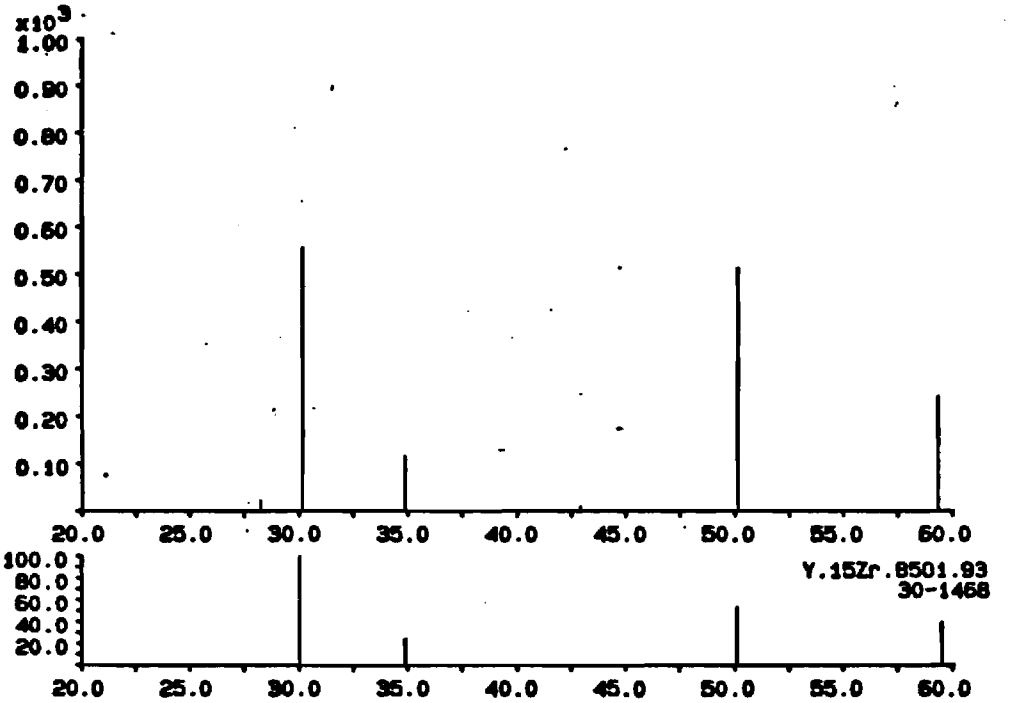


Figure 6. X-ray diffraction pattern of 4.5 mol% yttria-doped zirconia compared to 15 mol% yttria-doped zirconia.

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