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Cathode Dissolution

Quarterly Report, January-March 1987

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D.A. Shores

July 1987

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For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Minnesota Corrosion Research Center
University of Minnesota
Minneapolis, Minnesota

MASTER

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CATHODE DISSOLUTION

QUARTERLY PROGRESS REPORT #1

EXECUTIVE SUMMARY

During the report period subcontracts with Illinois Institute of Technology and with the Institute of Gas Technology have been set up, and graduate students have been recruited. The contractual requirements of preparing a Management Plan and a Test Plan have been completed. The design, construction (or purchase), and assembly of experimental apparatus is underway for Tasks 3, 4.1 and 4.2, which are concerned with the chemistry and kinetics of the dissolution of NiO. Initial considerations of a model of cathode dissolution processes, Task 5.1, is also underway. There was no planned activity in Task 5.2, in-cell tests of cathode degradation.

INTRODUCTION

One important mode of degradation of current MCFCs is the dissolution of the NiO cathode into the electrolyte tile and the subsequent precipitation of Ni in the tile. Over time the performance of the cell degrades, and eventually the cell may short out locally via a bridge of Ni particles between the cathode and anode. There is at present insufficient information to understand the cathode degradation processes in the detail needed to construct a comprehensive model. Such a model should be able to predict endurance or performance or to provide guidance for operating cells in a manner that would minimize the rate of degradation.

The purpose of this program is to further the understanding of the processes which cause degradation of the NiO cathode in MCFCs, especially those processes involving dissolution of the cathode and the transport of soluble Ni species in the electrolyte. The research work is divided into five tasks involving personnel at the Minnesota Corrosion Research Center (MCRC), Illinois Institute of Technology (IIT) and the Institute of Gas Technology (IGT). Both experimental measurements and modeling studies are being carried out. The five research tasks are as follows:

- Determination of the solubility of NiO in mixtures of molten carbonates (MCRC)
- Determination of the rates and mechanisms of NiO dissolution (MCRC)
- Determination of NiO reduction reactions (IIT)

- Modeling of cathode dissolution processes (IIT, joint with MCRC and IGT)
- In-cell tests to measure cathode dissolution and transport (IGT)

TECHNICAL PROGRESS

During this reporting period a revised Management Plan (Task 1) and a Test Plan (Task 2) were submitted to the COTR. Formal sub-contracts with the Illinois Institute of Technology for Task 4.2 NiO Reduction Reactions and Task 5.1 Modeling of Cathode Dissolution Processes and with the Institute of Gas Technology for Task 5.2 In-cell Cathode Dissolution and Transport were established. In addition a computer mail connection, via "BITNET", has been established with IIT to facilitate written communications. Activities in each task are summarized below.

TASK 3.0 THERMODYNAMIC SOLUBILITY OF NiO

The purpose of this task is to measure the thermodynamic solubility of NiO in molten carbonate mixtures relevant to fuel cell operations, and to determine the basicity of binary carbonate mixtures using an EMF cell technique. The basicity of a binary carbonate melt is a function of its composition and the partial pressure of CO₂ with which it is equilibrated.

Solubilities will be determined as a function of the gas composition variables to provide data from which the dissolution reaction can be inferred. Essentially, the slope of a plot of log [Ni] vs log [basicity] is a measure of the stoichiometric coefficients of the dissolution reaction. In a similar way, the effect of H₂O and the inferred dissolution reaction associated with H₂O, will be studied.

A schematic diagram of the experimental setup for solubility measurements is shown in **Figs. 1 and 2**. The details of the environments and temperatures for the NiO solubility measurements have been described in some detail in the "Test Plan". **Table 1** is reproduced from that document. In general, most tests will be carried out at 650°C. The gases will contain CO₂-O₂-Ar and some will also contain controlled concentrations of H₂O. The CO₂ concentration will be varied to establish conditions for either acidic or basic dissolution reactions. The H₂O will be varied systematically, at a fixed CO₂ activity, to determine the dissolution reaction.

In outline form the procedure for carrying out a solubility run is as follows:

Setup and Preparation

- Sample preparation
 - sinter NiO pellet
- Calibrate flowmeters
- Calibrate water vapor transpiration setup
- Choose gas composition
- Choose melt composition
- Set up furnace/gas train (Fig. 1)
- Prepare Ni standard solutions for spectrophotometric analysis

Equilibration Run

- Load sample and salt into furnace (Fig. 2)
- Establish gas flow
- Bring furnace to temperature
- Sample melt periodically to establish when equilibrated
- Take sample for Ni analysis and check analysis of alkali metals
- Change to new gas composition and repeat above steps
- Load new sample and run duplicate tests

Analysis of Melt

- Dissolve salt in acid solution
- Run spectrophotometric analysis of Ni against standards
- Check solvent melt by AA analysis of alkali metals

The EMF measurements involve a cell comprised of a gold wire (oxygen electrode) in a ZrO_2 tube and a gold wire in a mullite tube, both dipping into the melt of interest. The environment over the melt and inside the tubes will be controlled. A schematic diagram of the cell is shown in Fig. 3. The cell emf, after correction for a membrane potential, is a measure of the basicity of the melt. This technique has been applied to similar melts at a higher temperature by a previous student, and the present work will build upon this experience.

A graduate student, Mr. Gang Zhao, has been recruited for this task. He has begun by reading pertinent background information on fuel cells, especially "Assessment of Research Needs for Advanced Fuel Cells", which gives a very good overview of MCFC design and technology. The PhD thesis of a recent graduate, who measured NiO solubilities at high temperature, has been helpful in designing experiments and analysis schemes. He has further begun to design the

experimental setup for the solubility measurements and to assemble equipment. Some of the equipment needed for this work is available from that earlier study; other equipment, including a controlled temperature water bath for introducing known water vapor concentrations to the gas stream and a gas mass flow controller, have been purchased.

TASK 4.1 NiO DISSOLUTION RATE MEASUREMENTS

The purpose of this task is to identify and describe which of the several possible chemical and /or transport processes are the rate limiting step(s) for the dissolution of NiO in molten carbonates under conditions relevant to molten carbonate fuel cells. These conditions include gas composition, melt composition, temperature and potential. (The next task will consider electrochemical aspects of the dissolution process.)

This task focuses primarily on mass transfer processes. The rate of dissolution of NiO into molten carbonate melts will be determined by measuring the soluble Ni content in a known volume of melt as a function of time using analytical procedures as discussed for Task 3.0. To quantify mass transfer conditions, the NiO pellet will be fixed to the end of a rotating rod, which dips into the surface of the melt. The flow of salt past the NiO rod as a function of rotation speed can be estimated reasonably well from standard hydrodynamic correlations. Therefore, dissolution rates will be measured as a function of rotation speed to assess the hypothesis of mass transfer control. This experiment will be carried out for several sets of melt/environmental parameters, as shown in **Table 2**, which is taken from the "Test Plan". The solubility measurements in Task 3.0 will provide considerable helpful input in selecting critical melt/environmental parameters. It should be recognized that these experiments are difficult and time consuming, and a significant effort must be denoted to preliminary verification experiments.

A graduate student, Mr. Yingtze Qu, has been recruited for this task. He, like Mr. Zhao, has been reading background material and taking courses. He has also been working on the design of the apparatus, some of which will be purchased, and some will be built in our shop. A schematic diagram of the apparatus is shown in **Fig. 4**. It is not complete at this time.

TASK 4.2 REDUCTION REACTIONS ON NiO

The principal purpose of this task is to evaluate the effect of cell potential on NiO dissolution reactions and processes. This will be carried out with the use of two test setups involving thin electrolyte layers. The design and construction of the specialized cells comprise a significant portion of the effort. Schematic diagrams of the test cells are shown in **Fig. 5 and 6**. Table 3, reproduced from the "Test Plan", describes the proposed test variables.

Designs for a thin-layer cell and for a NiO-coated porous gold cathode have been prepared. The thin-layer cell has a flat horizontal nickel-oxide coated electrode completely covered by a thin layer of electrolyte. The layer is in liquid contact with a larger amount of bulk electrolyte through a diffusion barrier of e.g., mullite. This design, and especially the specifications of the diffusion barrier, are being checked with experts in the corrosion of ceramics by carbonate melts.

The NiO-coated porous gold cathode will consist of a number of gold mesh screens stacked together and compressed as a cathode in a 3-cm² cell. Preliminary experiments with Ni coating on gold wire are under way.

A graduate student, Mr. Suresh L. Israni, has been recruited to work on Tasks 4.2 and 5.1.

TASK 5 DISSOLUTION PROCESSES IN A MCFC CATHODE

The purpose of this task is to develop and test a theoretical model to describe the cathode degradation processes and to provide some predictive capabilities. The first task (5.1) is to establish the mathematical description of the dissolution processes that occur on a fuel cell cathode during cell operation. The model will incorporate as inputs the experimental dissolution rates and the effect of cell potential on dissolution rates, as well as other data on physico-chemical properties and processes that are available from the literature. Using these data the model will then attempt to describe the dissolution processes in a fuel cell. These predictive capabilities will be tested in the second task, which is to operate cell tests under conditions that are expected to accelerate cathode deterioration. A post-test analysis of cell components will be

compared with the predictions to verify the model. The overall progress of the model development will be one of incremental evolution and refinement as additional data (including the results of cell tests in Task 5.2) becomes available.

TASK 5.1 MATHEMATICAL MODELING OF NiO DISSOLUTION PROCESSES in MCFC

A modification of the agglomerate model developed by Yuh and Selman (C.Y. Yuh, Ph.D. Thesis, 1985) is being used to represent NiO dissolution in the cathode. The connection between the dissolution process within the cathode and the transport process in the tile has been formulated in a set of model equations. The numerical solution of these equations is being explored with a view to physically justifiable assumptions.

An important unresolved question basic to the model is the exact role of electrochemical dissolution reactions (anodic or cathodic) in the porous electrode. In the model equations, a corrosion (mixed potential) mechanism has been adopted. However, this is in apparent contradiction with the few thermodynamic data available for NiCO_3 and NiO . From these data it appears that

is thermodynamically unfavored. On the other hand,

may proceed as a parasitic reduction reaction in the MCFC under load. This issue continues to be studied.

TASK 5.2 IN-CELL CATHODE DISSOLUTION AND TRANSPORT

The purpose of this task is to support the modeling effort under Task 5.1 with experimental in-cell cathode degradation data. During the first fiscal year of the program, IGT will provide IIT with existing cathode data for drafting the preliminary dissolution model under Task 5.1. Toward the end of the first fiscal year, a joint meeting will be held by all participants to decide the final test conditions for the in-cell tests, based on preliminary experimental results under Tasks 3.0, 4.1, and 4.2 and the modeling effort under Task 5.1. Cell tests will be conducted during Year 2 of the project in laboratory-scale (3-cm³) fuel cells at IGT. The cell test stands will be modified as necessary to accommodate special test conditions. There has been no activity in Task 5.2 during the current reporting period.

TABLE 1
TEST CONDITIONS FOR NiO SOLUBILITY MEASUREMENTS*

Series	Melt	Temperature	CO ₂ ^a	O ₂ ^b	H ₂ O	No. of Tests
NS-A	62 Li/38 K	650	8	1	Fixed (-0)	8
NS-B	62 Li/38 K	600-780 (4)	2	1	Fixed (-0)	8
NS-C	62 Li/38 K	650	2	4	Fixed (-0)	8
NS-D	62 Li/38 K	650	2	1	8	16
NS-E	62 Li/38 K	600-780 (4)	1	1	2	16
NS-F	80 Li/38 K	650	8	1	Fixed (-0)	8
NS-G	80 Li/38 K	650	2	1	8	16
NS-H	43 Li/38 K	650	8	1	Fixed (-0)	8
NS-I	30 Li/38 K	650	8	1	Fixed (-0)	8
NS-J	30 Li/38 K	650	2	1	8	16
NS-K	100 NA	910	2	1	8	16
NS-L	52 Li/48 Na	650	8	2	Fixed (-0)	16
NS-M	52 Li/48 Na	650	2	1	8	16
NS-N	Ternary Eutectic	650	8	2	Fixed (-0)	16
NS-O	Ternary Eutectic	650	2	1	8	16

Notes:

- a These are the number of different gas compositions to be used.
When two values of CO₂ are indicated, then one value will be on the acid side and one on the basic side.
- b When one value is specified, then O₂ = 0.25 atm.

*The test conditions are described in order of priority. We will carry out as many tests as time permits.

TABLE 2
TEST CONDITIONS FOR TASK 4.1

Series	Melt	Temperature	CO ₂ ^a	O ₂ ^b	H ₂ O	No. of Tests
DK-A	62 Li/38 K	650	2	4	fixed (=0)	8
DK-B	62 Li/38 K	650	2	1	4	8
DK-C	62 Li/38 K	600-780 (4)	2	1	1	8
DK-D	100Na	910	2	1	fixed (=0)	2
DK-E	TBS(a)	650	2	1	1	N/A

Notes:

a Melt composition and parameters to be selected (TBS) to test preliminary hypotheses about the rate limiting steps.

TABLE 3
TEST CONDITIONS FOR TASK 4.2

Test #1 THIN-LAYER CELL TESTS FOR NiO DISSOLUTION (see Fig. 5 for cell configuration)

Melt	:	62 Li/38 K			
Temperature	:	650 C			
Gas composition	:	CO ₂	O ₂	N ₂	H ₂ O
	(a)	30	15	55	0
	(b)	67	33	0	0
	(c)	30	15	55	(sat 75C)
Potential (Load)	:	(A) open circuit			
		(B) maximum polarization of NiO electrode			

Analysis : Ni content of electrolyte (spectrophotom).

Test #2 POROUS GOLD/NiO CATHODE IN-CELL TESTS (see Fig. 6 for cell configuration)

Melt	:	62 Li/38 K			
Temperature	:	650 C			
Gas composition	:	CO ₂	O ₂	N ₂	H ₂ O
	(a)	30	15	55	0
	(b)	67	33	0	0
	(c)	30	15	55	(sat 75C)
Potential (Load)	:	(A) open circuit			
		(B) maximum polarization of NiO electrode			

Analysis : Ni content of electrolyte (spectrophotom).

Experimental setup for the solubility of NiO in molten carbonate

Figure 1 Schematic diagram of experimental arrangement for conducting NiO solubility measurements.

Figure 2 Schematic diagram of equilibration setup for making NiO solubility measurements.

Figure 3 Schematic diagram of electrochemical cell for making basicity measurements in binary carbonate mixtures.

Schematic of experimental equipment

Figure 4 Schematic diagram of cell, furnace and rotator (commercial unit to be obtained from Pine Instruments) for measuring the rates of NiO dissolution in molten carbonate salts with a. controlled environment.

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Figure 5 Schematic diagram of MCFC for TASK 4.2, test #1
(reproduced from "Test Plan")

Figure 6 Schematic cell arrangement of thin layer cell for TASK 4.2, Test #2. (The Al_2O_3 tube is closed by a gas-tight header plate with feed-throughs, which is not shown. (reproduced from "Test Plan")