DOE/MC/23264--3

DE-AC21

DE92 017546

DETERMINATION OF OPTIMUM ELECTROLYTE COMPOSITION FOR MOLTEN CARBONATE FUEL CELLS

QUARTERLY TECHNICAL PROGRESS REPORT

October, 1986 - December, 1986

Prepared by

ENERGY RESEARCH CORPORATION
3 Great Pasture Road
Danbury, CT 06813

A. Pigeaud
Principal Investigator

Prepared For

UNITED STATES DEPARTMENT OF ENERGY
Morgantown Energy Technology Center
3610 Collins Ferry Road
Morgantown, WV 26507-0880
F. Gmeindl, Technical Representative

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

DISCLAIMER

MASTER

Work Performed Under Contract No. DE-AC21-86MC23264

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

APPROVED FOR PUBLICATION
BY *[Signature]* DATE *7/28/92*

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States nor any agency, thereof, nor any of its employees, nor any of its contractors, subcontractors, or their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use or the results of such use of any information, apparatus, product or process disclosed in this report or represents that its use by such third party would not infringe privately owned rights.

TITLE: Determination of Optimum Electrolyte Composition
for molten Carbonate Fuel cell.

CONTRACT NO.: DE-AC21-86MC23264

CONTRACTOR: Energy Research Corp.
3 Great Pasture Road
Danbury, CT 06813

CONTRACT PERIOD October 1, 1986 to September 30, 1988

OBJECTIVE: The objective of this study is to determine the optimum electrolyte compositions for molten carbonate fuel cells. To accomplish this, the contractor will provide:

1. Comprehensive reports of on-going efforts to to optimize carbonate composition.
2. A list of characteristics affected by electrolyte composition variations (e.g. ionic conductivity, vapor pressure, melting range, gas solubility, exchange current densities on NiO, corrosion and cathode dissolution potential:
3. Assessment of the effects these characteristics have on state-of-the-art cell voltage and lifetime.

CONTRACT TASKS:

- Task 1. Preparation of Management Plan.
- Task 2. Literature Survey to review completed and ongoing efforts to optimize MCFC electrolyte composition.
- Task 3. Electrolyte Composition Screening to define "Optimum" in terms of carbonate properties and fuel cell parameters.
- Task 4. Test Plan submission describing methods to be used for identifying and verifying the optimum composition criteria.
- Task 5. Experimental Determination of Optimum Electrolytes by a variety of out-of-cell and in-cell tests.

PROGRESS BY TASK:Task 1 - Preparation of Management Plan

The Management Plan for this project was completed and was accepted after minor modifications were made. The overall approach for this study is shown in Figure 1.1. Experimental criteria for the selection of an "optimum" composition were developed and a preliminary tabulation was provided in our second report. This will be further developed as more insight is gained in the course of our literature search. Further discussion of the criteria will appear under Task 2.

Task 2 - Literature Survey

In a Molten Carbonate Fuel Cell (MCFC) all the components, including the internal and external surfaces of the bipolar plates, are wetted and coated with a thin film of molten carbonate electrolyte. Therefore the composition of the melt at any location impacts on all the various functions of the cell's active components such as the electrolyte matrix material, the electrodes, the cell hardware and any catalyst structures present.

Accordingly, a literature search matrix has been established to provide a well-defined listing of the most important characteristics to be surveyed under six different categories. In order to further focus our survey, each major category is again broken down into a small number of subjects presently considered to be of importance:

FIGURE 1.1 APPROACH FOR OPTIMIZING ELECTROLYTE COMPOSITION

2.1 Search Matrix

- General Criteria; includes relevant physical property data for different carbonate electrolyte mixtures which directly influence interactions with MCFC components.
 - Cell Performance in different Melts
 - Mixture Ionic Conductivities
 - Eutectic and off-Eutectic Melting Points
 - Mixture Vapor Pressures and various Gas Solubilities
 - Mixture Free Energies and Component Activities
 - Volume Expansion Coefficients (α and β)
- Corrosion; primarily metal loss with formation of mostly lithium oxide-scale causing loss of electrolyte and increases in contact resistance between components.
 - Scale Growth Mechanism affected by different melts (fluxing)
 - Metal Loss of Standard Alloy in different melts
 - Thermal and Current Flow Effects on Metal Loss
 - Effects on Pure Nickel
- NiO Stability; includes the major problem of bulk cathode loss through dissolution and migration of Ni species.
 - Dissolution Mechanism affected by Temperature/Pressure and Acid/Base conditions.
 - Effect of Redox and Potential Gradients in Electrolyte (Cathode to Anode)
 - Acid/Base Conditions effected by Gas Environment (CO_2 and H_2O primarily), other Alkalies (Na) and Additives (Mg, etc.)
 - Cathode Structural and Porosity Stability in different mixtures

- Cathode Kinetics; primary limitation on overall cell performance (voltage under high load).

- Gas and Ion mass Transport in Porous NiO structures
- Porosity Changes with time (ripening)
- Exchange Current densities and Tafel slopes with porous electrodes
- Simulted In-cell Impedance Studies
- NiO semiconduction depending on equilibrium lithium content

- LiAlO₂ Stability; primarily particle growth and changes in allotrope phase composition affecting electrolyte content and matrix conductivity.

- Allotrope conversion as a function of alkali cation ratios
- Crystal growth effects in different melts (ripening)
- Partial conversion to NaAlO₂ in high Na melts.

- Electrolyte Loss and Migration; constitutes the important contributions to cumulative changes in quantity and compositions of electrolyte remaining in active cell components.

- Wettability (Contact Angle) in different melts
- Cation segregation as a function of Corrosion, Volatility, Creep and Electrochemical Transfer
- Implications of Electrolyte Vaporization on MCFC Internal Reforming Catalysts

2.2 Literature Sources and Analysis

In addition to the in-house files of MCFC and related literature sources, the Molten Salt Data Center (MSDC) at Rensselaer Polytechnic Institute will be utilized. Contact has already been made and the search has been initiated. Papers pertinent to fundamental properties and interactions between carbonate melts and fuel cell components will be surveyed. A listing of the critical physico-chemical properties of relevant melts has also been updated as shown in Table 2.1. This listing derives primarily from a comprehensive survey of carbonate melt characteristics⁽¹⁾ which was completed in late 1976. That survey contains a large bibliography which encompasses a 50 year period and contains over 250 references. It will form the basis for our continued but much more electrolyte composition focussed search of the literature over the last 10 years.

Furthermore, a request for current information on electrolyte composition related results is being developed and has been sent to several DOE contractors and organizations involved in MCFC research. Work was also initiated to explore the possibility of defining a "characteristic" index for the behavior and reactivity of various melts. Such a characteristic, if definable, will be very useful in correlating the available physico-chemical properties of different melts that influence the solubilities and actual electrode kinetics, etc. in a molten carbonate fuel cell.

2.3 Selection Criteria for Electrolyte Composition

The considerations for selection of an optimum electrolyte composition are generally performance- , endurance- , and cost related. As will be shown below,

Table 2.1

LISTING OF CRITICAL ELECTROLYTE MIXTURE PROPERTIES

(Li, Na, K Carbonate Blends generally @ 650°)

Intrinsic Physico/Electro/Chemical and Thermodynamic

- Melting Points (Eutectic, Congruent, and Off-eutectic), °C
- Equivalent Melt Conductance (Total), S/cm
- Density, g/ml
- Viscosity over a range of $\pm 100^\circ\text{C}$, cPoise
- Individual Cation/Anion Diffusion Coefficients, cm^2/sec
- Individual Cation/Anion Activity Coefficients, $a=\gamma C$
- Volume Expansion Coefficients (s and ℓ), $10^{-6} \text{v/v}\cdot\text{K}$
- Phase Expansion upon Fusion (s $\longrightarrow \ell$), 10^{-6}v/v
- Surface Tension on Polished SS, dyne/cm
- Thermal Conductivity, $\text{W/K}\cdot\text{m}\cdot\text{s}$

In conjunction with different gases and solids

- Equivalent Vapor Pressures in Different Atmospheres
(e.g. $\text{MOH}_{(\text{v})}$ and $\text{K}_{(\text{v})}$ species), 10^{-6} atm.
- Gas Solubilities (H_2 , O_2 , CO_2 , N_2 , etc.), $\text{M/ml}\cdot\text{atm}$
- Diffusivities of these Gases, cm^2/sec
- Solid Solubilities ($\text{NiO}[\text{Li}]$, LiFeO_2 , LiCrO_4 , etc.), ppm
- Diffusion Coefficients for $\text{Ni}^{\text{II}}/\text{NiO}$; $\text{Fe}^{\text{III}}/\text{LiFeO}_2$;
 $\text{Cr}^{\text{IV}}/\text{LiCrO}_4$, etc.), cm^2/sec
- Relative Cation/Anion Activation Energies in Different Melts
(e.g. $\text{M}^+ + \text{XO} \longrightarrow \text{MXO}$; $\text{M}^+ + \text{X} \longrightarrow \text{MX}$; $\text{CO}_3^= + \text{Y} \longrightarrow \text{YO} + \text{CO}_2$), kJ/M
- Metal Loss (Oxidant Corrosion of a Standard Alloy), $\mu\text{m}/\text{yr}^{\frac{1}{2}}$

performance improvements⁽²⁾ of approximately 10% may be possible by optimizing the electrolyte. This would have a considerable impact on the economics of the molten carbonate fuel cell as an energy converter. In this preliminary study a few years ago performance improvements, as demonstrated by changes in overall cell resistance, were only correlated with known melt conductivities. It may very well be, however, that other contributing causes to improved cell performance are better gas solubility, better ionic diffusion and electrochemically more active species as well as lower viscosity of the melt, etc., all of which might influence cathode and anode kinetics besides the melt conductivity.

Endurance related parameters influenced by electrolyte composition are generally not immediately evident but could constitute a major consideration in the composition selection process. If cell or stack life is shortened through such factors as hardware corrosion, increasing contact resistance or porosity deterioration, this also could have an impact on the economics of fuel cell operation. Other factors that may affect life performance of a fuel cell could be through such mechanisms as electrolyte loss by vaporization or creep, loss of bulk cathode material through dissolution as well as impairment of the structural strength of the electrolyte matrix.

Cost-related parameters are usually closely intertwined with performance and endurance in that frequently there are certain 'material' solutions available, but these often come at a prohibitive cost. In general, the important factors are the cost of nickel and the stainless steel used in bipolar plates while the cost of lithium compounds is a much smaller factor. Among these material costs the need for highly corrosion resistant, stainless steel is probably particularly influenced by the choice of electrolyte composition.

2.3.1 Cell Performance, f(Electrolyte Composition)

Nine electrolyte compositions with promising characteristics were identified some years ago at IGT⁽³⁾ and ERC⁽⁴⁾. Comparative performance tests in laboratory scale cells were operated by both groups as discussed in the previously mentioned review by Maru et al⁽¹⁾. An essentially parallel correlation was established when correlating the cell resistance characteristics for eight of these cells vs. the intrinsic conductivity of the melts used. Accordingly, the quantitative improvement potentially available in MCFC performance with sodium containing blends (including both binary and ternary melts) as compared to our present compositions was estimated from 40 to 50 mV under high load conditions (200 mA/cm²). This estimate, as shown in Figure 2.1 and Table 2.2, has led to the desire for further research into additional properties and characteristics of sodium blends which might be either beneficial or not in other important performance or endurance related aspects.

MD0193

FIGURE 2.1 CELL RESISTANCE VS ELECTROLYTE CONDUCTIVITY CORRELATION
FOR MOLTEN CARBONATE FUEL CELLS AT 925K

TABLE 2.2
PERFORMANCE/CONDUCTIVITY/ELECTROLYTE COMPOSITION COMPARISON IN 8 LAB-SCALE CELLS

Blend Indices	Mole % Comp'n Li/Na/K	650°C Calculated Blend Conductivity, (S/cm)	Total Cell Performance, mV 400 hrs. 700 hrs.	Area Specific Resistance $\Omega \cdot \text{cm}^2$	IR-corrected Performance, mV
I	50 — 50	1.2	* 830 ⁺	0.50	899
II	62 — 38	1.4	790	0.50	847
III	63 — 37	1.4	870	0.48	947
IV	43 33 24	1.5	680	0.57	771
V	68 — 32	1.6	770	0.45	822
VI	77 — 23	1.8	903	0.48	980
VII	57 31 12	1.8	912	0.45	984
VIII	52 48 —	2.1	883	0.36	940
*IGT test conditions: 80% H ₂ /20% CO ₂ with 7.5% fuel utilization; 70% Air/30% CO ₂ with 15% O ₂ utilization measured at 160 mA/cm ²					
+ERC test conditions: 80% H ₂ /20% CO ₂ with 30% fuel utilization; 70% Air/30% CO ₂ with 30% O ₂ utilization measured at 115 mA/cm ²					

REFERENCES

As this study progresses, reference will be made to numerous literature sources that are surveyed for relevant information. For simplicity, this section will be carried forward in each report as further additions are made to it but without any changes being made in the numerical sequence.

1. Maru, H.C., Pigeaud, A., Ong, E., Selman, J.R., Marianowski, L.G. et. al.; "Fuel Cell Research on Second Generation Molten-Carbonate Systems: Vol. II Characteristics of Carbonate Melts", IGT Quarterly Status Report for DOE/ANL under contract No. 31-109-38-3552 (July-Sept., 1976)
2. Maru, H.C., Paetsch, L., and Pigeaud, A.; "Review of Molten Carbonate Fuel Cell Matrix Technology," Proc. Symposium on MCFC Technology, The Electrochemical Society, Inc. Vol. 84-13, Pennington, N.J. (1984)
3. Marianowski, L.G.; "Fuel Cell Research on Second-Generation Molten-Carbonate Systems," IGT Final Report for DOE Contract No. EC78-C-03-1735 (Oct. 77 - Sept. 78)
4. Pigeaud, A.; "Development of MCFC Technology," ERC Annual Report for DOE Contract No. DE-AC03-76ET11304 (Feb. - Dec., 1980)

DISTRIBUTION

- A. U.S. Department of Energy
Morgantown Energy Technology Center
ATTN: F. Gmeindl (cc: John Young, ANL - 1 copy)
P.O. Box 880, 3610 Collins Ferry Road
Morgantown, WV 26507-0880
(1 copy)
- B. U.S. Department of Energy
Morgantown Energy Technology Center
ATTN: Contractor Reports Receipt Coordinator,
M/S 105 (T-44)
P.O. Box 880, 3610 Collins Ferry Road
Morgantown, WV 26507-0880
(4 copies)

END

**DATE
FILMED
9/02/92**