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DETERMINATION OF OPTIMUM ELECTROLYTE COMPOSITION FOR MOLTEN CARBONATE FUEL CELLS

QUARTERLY TECHNICAL PROGRESS REPORT

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TITLE: DETERMINATION OF OPTIMUM ELECTROLYTE
COMPOSITION FOR MOLTEN CARBONATE FUEL CELL

CONTRACT NO.: DE-AC21-86MC23264

CONTRACTOR: Energy Research Corp.
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CONTRACT PERIOD: October 1, 1986 to September 30, 1988

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

1. Comprehensive reports of on-going efforts 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.

TASK 1 PREPARATION OF MANAGEMENT PLAN

The management plan has been submitted to DOE/COTR and has been approved. This task is complete.

TASK 2 LITERATURE SURVEY

The most recent information available on MCFC Corrosion, NiO dissolution, and Cathode kinetics, as well as LiAlO₂ stability, Electrolyte migration and Carbonate Conductivity has been thoroughly reviewed. A draft Topical Report was submitted to DOE/COTR in April, containing all the updated information and discussing the methods to be used to fill in existing information gaps. This task is therefore practically complete although future publications and further data coming available will continue to be reviewed and used in the electrolyte optimization process. Some efforts will therefore continue under this task but at a much reduced level.

TASK 3 ELECTROLYTE COMPOSITION SCREENING

Based on our best recent data and new information from various literature sources a preliminary set of 5 carbonate compositions has now been selected as shown in Table 3.1. These compositions are relatively firm choices for our initial test program but can still be adjusted before in-cell testing begins.

The basic concept is to compare the different electrolyte compositions with the one well-characterized "standard" of 62Li/38K carbonate which is the mixture shown as Code S. Table 3.1 presents preliminary valuations and comparisons for the selection of the present 5 compositions. A predetermined weighting of these criteria has already occurred because initial or primary selection is to be made on the basis of the first two major decisions which are NiO-solubility affecting the cathode loss parameter and corrosion expressed in terms of loss of 310S stainless steel thickness. This will narrow the number of compositions from 5 to 3 candidate

TABLE 3.1 A PRELIMINARY LIST OF CANDIDATE ELECTROLYTE COMPOSITIONS

CODE	TYPE	Li/Na/K (Mole %)	MELT. POINT °C	CONDUCTIVITY AT 650°C (Ω-cm) ⁻¹	Na LOSS μg/hr. cm ²	310-S METAL LOSS μm/(yr) ^{1/2}	CATHODE IMPEDANCE (Ω. cm ²)	ELEC- TROLYTE VAPOR LOSS μg/cm ² ·hr	ELECTROLYTE MIGRATION (EST.)	LiAlO ₂ STABILITY, REMAINING BET. m ² /g
S	STANDARD Li/K BINARY, EUTECTIC-2	62/-/38	490	1.4	HIGH (4-5)	-40 (3.5 mil in 40,000 hrs)	LOW	0.75 (K VOLA- TILITY)	K MIGRATES FASTER	4-5
S _L	Li/K BINARY, HIGH LITHIUM OFF-EUTECTIC	72/-/28	575	1.7	LOW (2-3)	MEDIUM	LOW	MEDIUM	MOBILITY OF Li, K SIMILAR	SIMILAR
N _L	Li/Na BINARY, SLIGHTLY OFF- EUTECTIC	60/40/-	540	2.3	LOW (-3)	UNKNOWN	MEDIUM	LOW	UNKNOWN	UNKNOWN
S _H	Li/K BINARY + ADDITIVE (0.5 Mg)	62/-/38	(490)*	(1.4)*	MEDIUM -LOW (2-3)	MEDIUM -LOW	LOW	HIGH	UNKNOWN	UNKNOWN
S _X	Li/K BINARY + ADDITIVE (5 Ba or Sr)	59/-/36	(490)*	(1.4)*	MEDIUM -LOW (2-3)	MEDIUM -LOW	LOW	HIGH	UNKNOWN	UNKNOWN
ELECTROLYTE SELECTION									<10% CATION RATIO CHANGE	>5

* estimated value

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compositions. The possible effects of these different candidate electrolyte compositions on the important issues listed have been discussed in detail in our recent April Monthly Report.

Corrosion and NiO solubility in the five candidate melts will be evaluated by the primary screening process. According to the literature survey, the candidate electrolytes shown are not expected to greatly affect the rate of corrosion attack on 310S stainless steel. It is therefore expected that the best composition as a result of primary out-of-cell screening will be selected for its more effective suppression of NiO solubility. In the event of equal NiO solubility, a melt with higher electrolyte conductivity will, of course, be preferred. But if later a candidate electrolyte (possibly with a NiO-solubility preventive additive) is also able to significantly suppress corrosion, that would be very desirable too, even if not fully satisfying the NiO solubility criteria.

After primary screening, 3 melts will be selected for additional or secondary screening. In secondary screening, the order of importance for electrolyte selection is suggested to be: cathode performance > electrolyte migration > LiAlO_2 stability. Eventually, one optimum electrolyte composition from the remaining electrolytes will be selected for cell testing with possibly also some input from potential vapor loss calculations.

3.1 AC-IMPEDANCE TECHNIQUE: ELECTRODE KINETICS STUDY

The AC-impedance technique to be used in the electrode kinetic screening of candidate compositions has not been previously discussed in detail. The following is a general description of the fundamentals of AC-impedance analysis:

In the AC-Impedance Technique of electrochemical kinetics studies, a small AC signal is used to perturb an electrode/electrolyte system which is usually at its rest potential. The manner in which the system reacts to this perturbation is observed in terms of the current/voltage response over a wide frequency band which induces different phase lags between these two variables. This method has the following advantages over static polarization or resistance measuring techniques:

- 1) High precision measurements are possible because a stabilized response can be measured and averaged over a long period of time and,
- 2) Linearized electrode kinetics is used for the small perturbations which greatly simplifies theoretical analysis.

When a sinusoidal voltage input is applied to a system:

$$V = I_0 \bar{R} \sin(\omega t + \theta)$$

the corresponding current output due to this perturbation is:

$$I = I_0 \sin(\omega t)$$

where $\bar{R}$ is the magnitude of the resistance vector of the system and θ is the phase offset between current and potential cycles. In electrochemical systems this is usually expressed in terms of a negative phase shift with respect to current. The resulting impedance/admittance can be represented in polar form by:

$$Z = \bar{R} \cdot e^{i\theta}$$

or also in complex variable form (cf. Figure 3.1):

$$Z = a + bi$$

FIGURE 3.1 SCHEMATIC OF IMPEDANCE AND ADMITTANCE

Ideally, a planar electrode may be represented by the equivalent circuits and Nyquist diagrams shown in Figure 3.2. Only an algebraic manipulation is required to represent the double layer capacitance and resistances of the equivalent circuits as complex variable graphs. However, such simple systems rarely exist because the presence of surface adsorption, oxide and barrier films or surface roughness usually complicates the frequency response. Only simple redox systems (e.g. ferricyanide-ferrocyanide reacting on a smooth nickel electrode) can be approximated in such fashion.

Theoretical and experimental AC-Impedance analysis of porous electrodes has been employed by a number of researchers. A Literature Survey provided by Yuh in his thesis(16) lists some of the authors who have done research in this field. Yuh, in his work, has developed mathematical models for the analysis of AC-Impedance in 'porous' electrodes and was able to characterize an in situ oxidized, porous cathode in MCFC environment.

Rate-limiting processes were identified and useful kinetic information was obtained in these early studies.

FIGURE 3.2 SCHEMATICS FOR IDEALIZED PLANAR ELECTRODE SYSTEM

According to Yuh, the solution for the theoretical AC-impedance model of a porous electrode, including mass transfer is:

$$Z = R_s + \frac{H \coth(\sqrt{G})}{\sqrt{G}}$$

where $H = \frac{L}{A \cdot \bar{k}}$

Figure 3.3 shows schematically the types of responses that can occur according to this impedance model. Without charge transfer reaction, the Nyquist plot is the same as that predicted by deLevie (64) and Keiser et al. (65): a 45° asymptote at high frequencies and a 90° asymptote at low frequencies. The distance between the 90° asymptote and the imaginary axis is $R_s + \frac{H}{3}$. In the presence of a charge transfer reaction, the low frequency part has to approach the real axis. Furthermore the larger the charge transfer impedance, the smaller the angular frequency at the top of the Nyquist diagram. If mass transfer impedance is included, a secondary loop with a 22.5° slope also occurs at low frequencies.

Although this model is simple, it is capable of accurately describing the frequency response of a porous electrode at its equilibrium potential. The values of the exchange current density may be estimated directly from the size of the impedance loop. Thus, if there is no mass transfer resistance (e.g. the diffusivity is infinite), the solution of the above equation reduces to:

$$Z = \frac{H \coth(\sqrt{G_0})}{\sqrt{G_0}}$$

In many systems the parameter G_0 is large. Therefore $\coth(\sqrt{G_0})$ is approximately equal to 1, and the total impedance Z becomes:

$$Z = \frac{H}{\sqrt{G_0}}$$

FIGURE 3.3 TYPES OF AC-IMPEDANCE RESPONSE FROM SIMPLIFIED MODEL

If the above approximation is valid, there exist two ways of extracting the kinetic information directly from an experimental Nyquist diagram as shown in Figure 3.4, because 1) at very low frequencies, the kinetic impedance approaches $(R_s + \bar{a}, 0)$, and the local kinetic impedance can be determined; the drawback is that the existence of mass transfer at low frequencies, < 0.5 Hz, makes the extrapolation uncertain. And 2), at the maximum of the imaginary part of the loop, the total impedance

$$W = a i_0^b \bar{\kappa} \phi (\alpha_a + \alpha_c)$$

$\underline{A}$ = Crosssectional Area of the Electrode

FIGURE 3.4 TWO METHODS FOR DETERMINING THE SIZE OF A KINETIC LOOP

$Z = (R_s + \sqrt{3}\bar{b}, \bar{b})$ and the corresponding angular frequency equals $\sqrt{3} A'/C$. If the kinetic impedance is small, the angular frequency is large. Because the mass transfer impedance is only appreciable at low frequencies, impedance at the maximum of the imaginary part of the loop is free of a mass transfer component in this case. However, for a system with very large impedance, mass transfer resistance may still contribute, but only very little, to the predominant kinetic contribution. The height of the impedance loop should be proportional to the square root of the local charge transfer impedance. This allows one to deduce effects of gas composition and temperature on the process. Reaction orders and activation energies can also be determined.

For example, in an experimental analysis, the following procedure will be followed. About 15 frequencies between 0.1 and 2 kHz will be used for each measurement event though only data points for four typical frequencies (1, 10, 100, and 500 Hz) are normally indicated on experimental impedance diagrams. All the results are commonly obtained at electrochemical equilibrium; i.e. the system rest potential. Figure 3.5 shows a comparison of the experimental Nyquist diagrams for an anode and a cathode operated on "standard" fuel and oxidant gas, respectively.

FIGURE 3.5 FREQUENCY RESPONSE OF TYPICAL MCFC ANODE AND CATHODE

It is seen that the cathode impedance is much larger than that of the anode and has a fairly large double layer charging compared to transfer contribution even at 500 Hz. This is of course due to considerably slower kinetics at the cathode compared to the anode in the molten carbonate system. Another important observation is the apparent existence of a second (mass transfer) loop for the anode.

Several examples of AC-Impedance diagrams for the porous MCFC cathode (cf. Figures 3.6-3.8) further clearly indicate the strong effect of gas composition and temperature on cathode kinetics. The heights of the high frequency loops were correlated with respect to temperature and partial pressures of O_2 and CO_2 . Reaction orders and activation energies could thus be established.

FIGURE 3.6 EFFECT OF pCO_2 ON MCFC POROUS CATHODE IMPEDANCE

FIGURE 3.7 EFFECT OF $p\text{CO}_2$ ON MCFC POROUS CATHODE IMPEDANCE

FIGURE 3.8 EFFECT OF TEMPERATURE ON MCFC CATHODE IMPEDANCE

In this research, a Solartron 1250 Frequency Response Analyzer and a Solartron 1286 Electrochemical Interface are normally used for these AC-Impedance measurements. Data are collected with an HP-85 digital computer and the variables in the complex plane are directly graphed on an HP-plotter. The data are thus analyzed both as to ohmic resistivity and the various other parameters which can describe cathode kinetics or, depending on the cell configuration, in situ corrosion film formation. The ability to decide on the correct cell configuration to study a given electrochemical phenomenon is of course a major part of any investigation.

LIST OF SYMBOLS

a	Real Part of Impedance	$\bar{R}$	Magnitude Resistance Vector
$\bar{a}$	$1/(\sqrt{w} \cdot A)$	R_s	Solution Ohmic Resistance
$\underline{A}$	Crosssection Electrode Area	R_{ct}	Charge Transfer Resistance
A'	$i_0 (\alpha_a + \alpha_c) \phi$	R_w	Warburg Resistance
b	Imaginary Part of Impedance	t	Time
$\bar{b}$	$1/(\sqrt{8w} \cdot A)$	T	Temperature
C, C_d	Double Layer Capacitance	V	Voltage
F	Faraday Constant	w	$ai_0 \bar{\kappa} (\alpha_a + \alpha_c) \phi$
G	$a(A' + i\omega C) / (1 + Z_w A') (L^2 / \bar{\kappa})$	Z	Impedance
G ₀	$aL^2 / \bar{\kappa} (A' + i\omega C)$	Z_w	Warburg Impedance
H	$L / (\underline{A} \bar{\kappa})$	α_a	Anodic Transfer Coeff.
i	$\sqrt{-1}$	α_c	Cathodic Transfer Coeff.
i_0	Exchange Current Density	ϕ	F/RT
I ₀	Current	$\bar{\kappa}$	Eff. El'ctrlte Conductivity
L	Thickness of Electrode	θ	Phase Shift
R	Universal Gas Constant	ω	Angular Frequency

TASK 4 TEST PLAN AND CONDITIONS

The test plan for out-of-cell and in-cell testing has been almost finished. The plan describes test conditions, facilities, test methods, and post-test analyses for each of the out-of-cell and in-cell experiments. Critical values for making comparisons in terms of fuel cell parameters are also discussed. A draft test plan will be momentarily submitted to DOE/COTR for approval.

4.1 OXIDANT AND FUEL COMPOSITIONS

Generally 'system' oxidant and fuel compositions will be used in most of our screening tests. Table 4.1 illustrates the 'standard' system oxidant composition and two other gas compositions which are needed for particular test purposes.

TABLE 4.1

STANDARD OXIDANT COMPOSITIONS

	Vol. %			
	O ₂	CO ₂	H ₂ O	N ₂
System Oxidant	10	13	3	Balance
Noble Oxidant (Kinetics Diagnostics)	33.3	66.7	-	-
Oxidant A (to accentuate NiO-solubility)	10	85	5	-

In connection with the selection of a 'standard' fuel gas, representing either natural or coal-gas sources, various mixtures representing different systems and gasifiers have been evaluated with respect to their tendency for soot formation. Table 4.2 illustrates a typical UGAS air-blown product stream (also very similar to the Westinghouse Air-Blown Gasifier product) as it exits at high temperature from the gasifier. Were this gas not blended with additional steam, the water-gas equilibrated composition at 650°C fuel cell temperature represents a relatively severe soot forming compo-

TABLE 4.2
UGAS Air-blown (TRW report)

Gas	Gasifier Exit (dry gas)		To MCFC, humidified to 29% of feed gas
	Unequili- brated (%)	Water-gas (650°C) Equilibrated (%)	Water-gas (650°C) Equilibrated (%)
H ₂	13.2	11.1	17.0
CO	19.3	21.4	6.1
CO ₂	10.0	7.9	14.7
H ₂ O	—	2.1	21.4
CH ₄	4.7	4.7	3.3
N ₂	52.8	52.8	37.5

C/H/O ratios counting CH₄ as an inert
 (i.e. N₂-type diluent) gas

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dry		
C	H	O
30.6	27.8	41.4

humidified		
C	H	O
13.5	49.7	36.8

sition in terms of MCFC use. However, when up to 29% of steam is added to such a feed gas it is seen that, good stability in terms of potential soot formation can be achieved as well as providing an increased conversion to hydrogen.

Some 'standard' system and special purpose fuels that could be used in molten carbonate fuel cell and stack testing are illustrated in Table 4.3. System 6C fuel represents a Natural Gas fuel which clearly needs reforming as the kinetics of uncatalyzed methane decomposition has been found to be a much slower one than Water-gas equilibration at 650°C. The second very high hydrogen content fuel has been historically used in much of the early fuel cell development work to attain a high Nernst potential but this is not really a significant factor except diagnostically. The additionally humidified UGAS composition is a fairly typical coal-gas product from gasifiers operated under air-blown conditions and is suggested as the standard composition for our present work.

TABLE 4.3

STANDARD FUEL COMPOSITIONS

	Vol% (Water-gas equilibrated @ 650°C)					
	H ₂	CO ₂	CO	H ₂ O	CH ₄	N ₂
System 6C Fuel (Needs Reforming)	31.5	-	-	41	27.5	-
Historical HBTU Fuel (Kinetics, Diagnostics)	62	8	10	20	-	-
Coal-gasifier Fuel humidified (UGAS)	17	14.7	6.1	21.4	3.3	37.5

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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 and further additions will be made to it without changes in the numerical sequence.

1. Maru, H.C., Pigeaud, A., Ong, E., Selman, R.J., Marianowski, L.G. et al.; "Fuel Cell Research on Second Generation Molten-Carbonate Systems: Vol. II, Characteristics of Carbonate Melts", Quarterly Status Report (July-Sept.) for DOE/ANL Contr. No. 31-209-38-3552, Inst. of Gas Technology, Chicago, IL (1976).
2. Maru, H.C., Paetsch, L. and Pigeaud, A.; "Review of Molten Carbonate Fuel Cell Matrix Technology," Proc. Symp. on MCFC Technology; Electrochemical Society, Inc. 84-13, Pennington, N.J. (1984).
3. Marianowski, L.G.; "Fuel Cell Research on Second Generation Molten-Carbonate Systems," Final Report for DOE Cont. No. EC78-C-03-1735, IGT, Chicago, IL (Oct. '77 - Sept. '78).
4. Pigeaud, A.; "Development of MCFC Technology," Annual Report for DOE Contract No. DE-AC03-76ET11304, Energy Research Corp., Danbury, CT., Feb.-Dec. (1980).
5. Selman, J.R. and Maru, H.C.; "Physical Chemistry and Electrochemistry of Alkali Carbonate Melts," Advances in Molten Salt Chemistry, 4, p.159 and 330, Mamantov and Braunstein, eds., Plenum Press, NY, (1983).
6. Shores, D.A. and Singh, P.; "Hot Corrosion of Materials in Molten Carbonate Fuel Cells," Proc. Symposium on MCFC Technology, The Electrochemical Society, Inc., 84-13, Pennington, N.J. (1984).
7. Iacovangelo, C. et al.; Final Report for DOE under Contract No. DE-AC02-80ET17019, General Electric Co., Schenectady, N.Y., March (1985).
8. Yuh, C.Y. and Pigeaud, A.; "Corrosion Resistant Materials in MCFC Environments," Final Report to DOE under Contract No. DE-AC21-84MC21186, Energy Research Corp., Danbury, CT. Nov. (1986).
9. Paetsch, L., "Development of Molten Carbonate Fuel Cell Technology," Report No. 35 for DOE Contract No. DE-AC03-76ET11304, Energy Research Corp., Danbury, CT. Jan.-Mar. (1985).

ENERGY RESEARCH CORPORATION

10. Ibid., Report No. 32 (Apr.-June, 1984).
11. Ibid., Report No. 36 (Apr.-June, 1985).
12. Janz, G.J. et al.; "Physical Properties Data Compilation Relevant to Energy Storage." Molten Salts, Vol. II: Data on Single and Multi-Component Systems; National Bureau of Standards NSRDS-NBS 61, (1979).
13. Paetsch, L.; "Development of Molten Carbonate Fuel Cell Technology," Report No. 38 for DOE Contract No. DE-AC03-76ET11304, Energy Research Corp., Danbury, CT. Oct.-Dec. (1985).
14. Appleby, A.J. and Nicholson, S.B.; "Reduction of Oxygen in Alkali Carbonate Melts," J. Electroanal. Chem., 83, p.309 (1977).
15. Lu, S.H., "Electrode Kinetics of Fuel Oxidation and Oxygen Reduction in Molten Carbonate," Ph.D. Thesis, Illinois Institute of Technology, Chicago, IL (1985).
16. Yuh, C.Y., "Potential Relaxation and AC-Impedance of Porous Electrodes," Ph.D. Thesis, Illinois Institute of Technology, Chicago, IL (1985).
18. Uchida, I.; "Gas Electrode Reaction in MCFC," Fourth and other Reports of Special Project Research under Grant in Aid of Scientific Research of Ministry of Education and Culture, February (1984).
20. Appleby, A.J. and Nicholson, S.B.; "Reduction of Oxygen in Lithium-Potassium Carbonate Melt," J. Electroanal. Chem., 112, p.71 (1980).
21. Uchida, I., Nishina, T., Mugikura, Y. and Itaya, K.; "Gas Electrode Reactions in Molten Carbonate Media, Part I.: Exchange Current Density of Oxygen Reduction in (Li/K)CO Eutectic @650°C," J. Electroanal. Chem., 206, p.229 (1986).
22. Ibid., Part II: Oxygen Reduction Kinetics on Conductive Oxide Electrodes in (Li/K)CO Eutectic @650°C," J. Electroanal. Chem., 206, p.241 (1986).
23. Tang, T.E., Selman, J.R., Claar, T.D., and Marianowski, L.G.; "Effect of Oxidant Compositions on the Cathode Performance of a Molten Carbonate Fuel Cell," Abs. 3127, Extended Abstracts 80-2, Electrochem. Soc., Pennington, N.J. (1980).
24. Vogel, V.M., Bregoli, L.J., Kunz, H.R. and Smith, S.W.; "Stability of NiO Cathodes in Molten Carbonate Fuel Cells," Proc. Symposium on MCFC Technology, The Electrochemical Society, Inc., 84-13, Pennington, N.J. (1984).

ENERGY RESEARCH CORPORATION

25. Baumgartner, C.E., "NiO Solubility in Molten Li/K Carbonate under MCFC Cathode Environments," J. Electrochem. Soc., 131(8), p.1850 (1984).
26. Baumgartner, C.E.; "Solubility and Transport of NiO Cathodes in Molten Carbonate Fuel Cells," J. American Ceramic Soc., 69(2), p.162 (1986).
27. Doyon, J.D., Gilbert, T. and Davies, G.; "Dissolution of Nickel Oxide Cathodes in the Molten Carbonate Fuel Cell," submitted for publication to J. Electrochemical Soc. (1986).
28. Remick, R.J.; "Nickel Transport in Molten Carbonate Fuel Cell Electrolyte," Final Report for DOE Contract No. DE-AC21-85MC22224, Inst. of Gas Technology, Chicago, IL (1986).
29. Orfield, M.K. and Shores, D.A.; "The Dissolution of NiO in Molten Carbonate Mixtures," Paper 88, Annual Meeting, Corrosion-86, National Association of Corrosion Engineers (1986).
30. Orfield, M.K. and Shores, D.A.; "The Solubility of NiO in Molten Carbonate," Abstract 50, Extended Abstracts 84-2, The Electrochem. Soc., Pennington, N.J. (1984).
31. Nishikata, A. and Haruyama, S.; "Electrochemical Studies of Corrosion of Ni and Fe in Molten Carbonate", J. Japan Inst. Metals, 48(7), p.720 (1984).
32. Nishikata, A. and Haruyama, S.; "Electrochemical Monitoring of the Corrosion of Ni, Fe, and their Alloys in Molten Salts", Corrosion, 42(10), p.578 (1986).
33. Harada, H., Matsunaga, M. and Hosokawa, K.; "A Study on Electrochemical Reactions of Oxygen Species in Molten Carbonates", 19th Symp. Molten Salt Chemistry, B202, p.83, Electrochem. Soc. Japan, Osaka, Japan, November (1986).
34. Tanase, S., Miyazaki, Y., Yanagida, M., Tanimoto, K. and Kodama, T.; "Conductivity Measurements in Molten Alkali Carbonates", Progress in Batteries and Solar Cells, 6, p.195 (1987).
35. Vorob'ev, G.V., Pal'guev, S.F. and Karpachev, S.V.; Trud. Inst. Elektrokhim. Akad. Nauk SSSR Ural. Fil. 2, p.115 (1961).
36. Spedding, P.L.; "Electrical Conductance of Molten Alkali Carbonate Binary Mixtures", J. Electrochem. Soc., 120(8), p.1049 (1973).
37. Pal'guev, S.F. and Vorob'ev, G.V.; Trud. Inst. Elektrokhim, Akad. Nauk SSSR Ural. Fil. 2, p.121 (1961).

ENERGY RESEARCH CORPORATION

38. Noda, H., Shiota, K., Shiokawa, J., Tamura, H., and Ishino, T.; "Electric Conductance of Molten Alkali Carbonates", J. Electrochem. Soc. Japan, 31, p. 417 (1963).
39. Ward, A.T. and Janz, G.J.; "Molten Carbonate Electrolytes: Electric Conductance, Density and Surface Tension of Binary and Ternary Mixtures", Electrochimica Acta, 10, p.849 (1965).
40. Ota, K., Mitusima, S., Shinjo, T., Ouchi, T. and Kamiya, N.; "Solubility of Nickel Ferrite in Carbonate Melt," 19th Symposium on Molten Salt Chemistry, B205, p.89, Electrochem. Soc. Japan, Osaka, Japan (1986).
41. McCoy, L., and Schuman, M.; "Electrochemical Investigation of Lithium/Potassium Carbonate Eutectic for Application in Modeling the Molten Carbonate Fuel Cell Cathode," Final Progress Report for DOE, Contract No. DE-AC21-84MC21185, Rockwell International Corporation, California (1986).
42. Foote Mineral Company, "Lithium Aluminate for Fuel Cell and Ceramic Applications," Bulletin #155, FMC, Exton, PA 19341 (1986).
43. Broers, G.H.J. and van Ballegoy, H.J.J., "Phase Equilibria in Li-Na-K Carbonate/Aluminate Systems", paper presented at 3rd Int. Symp. on Fuel Cells, Brussels (1969).
44. Energy Research Corporation, "Molten Carbonate Fuel Cell Development," Final Report to U.S. DOE, Contract No. DE-AC03-76ET11304, April (1987).
45. Kaun, T.D., Fannon, T.M., and Baumet, B.A., "Solubility of Proposed Cathode Materials for Molten Carbonate Fuel Cells," Extended Abstract No. 52, 84-2, Electrochemical Society, Pennington, N.J. (1984).
46. Davtyan, O.K.; "Direct Conversion of Fuel Energy into Electricity", Bull. Acad. Sci. USSR, C1 Sci. Tech. p.215 (1946).
47. Shiota, K., Tamura, H. and Ishimo, T., "Studies on High Temperature Fuel Cells", Technology Report - Osaka Univ. 17, p. 748-768 and p. 183-191 (1967).
48. Millet, J. and Buvet, R., "Pile à Electrolyte Libre Alimentée en Air et Gas de Reformage", Revue Energie Primaire 1, p.49-53 (1965).
49. Tantram, A.D.S., "Operation of a Fuel Cell Containing Fused Metal Hydroxide and Carbonate Electrolyte", U.S. Patent 3,330,699 (1967).
50. Gorin, E. and Recht, H.L.; Chemical Engineering Progress 55, p.51 (1959).

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51. Schultz, E.B., Vorres, K.S., Marianowski, L.G. & Linden, H.R.; "Fuel Cells" (Young, G.J., ed.), 2, p.24-36, Reinhold, New York (1963).
52. Chambers, H.H. and Tantram, A.D.S.; "Fuel Cells" (Young, G.J., ed.), 1, p.94, Reinhold, New York, (1960).
53. Broers, G.H.J., Schenke, M. and Piepers, G.G.; Advanced Energy Conversion 4, p.131 (1964).
54. "A.G.A. Project DC 4-1"; Final Report, Institute of Gas Technology, Chicago (1967).
55. Hsu, H.S., and Howell, M.; "Corrosion of Fe-25Cr-20Ni Alloy in Molten Alkali Carbonates," Prepared by Oak Ridge National Laboratory for DOE, Contract No. DE-AC05-84OR21400, March (1987).
56. Maru, H.C., Pigeaud, A., Chamberlin, R. and Wilemski, G.; "Electrolyte Management in Molten Carbonate Fuel Cells," Proc. Symp. Electrochemical and Thermal Modeling; The Electrochemical Society, Inc. 86-12, p.398, Pennington, N.J. (1986).
57. General Electric Corp., "Development of Molten Carbonate Fuel Cell Power Plant," Final Report to DOE, Contract No. DE-AC02-80ET17019, March (1985).
58. Kodama, T., "Material Studies on Molten Carbonate Fuel Cell," Progress in Batteries & Solar Cells, Vol. 6, 7 (1987).
59. Murata, K., et al., "Molten Carbonate Fuel Cell," Japanese Patent 60-56375, Toshiba, Ltd. (1983).
60. United Technologies Corporation, "Development of Molten Carbonate Fuel Cell Power Plant Technology," Quarterly Progress Report to DOE under Contract DE-AC21-79ET15440, Jan.-March, 1985.
61. Kunz, H.R., "Binary Electrolyte for Molten Carbonate Fuel Cells," U.S. Patent 4591538 (1986).
62. General Electric, "Development of Molten Carbonate Fuel Cell Power Plant," Quarterly Progress Report to DOE under Contract DE-AC02-80ET17019, Feb.-April, 1982.
63. Hiroshi, F., Kiyoshi, H., and Takehiko, Y., "Alloys for Molten-Carbonate Fuel Cell Separators," Japanese Patent 61-216256, Hitachi, Ltd. (1986).
64. deLevie, R., "Electrochemical Responses of Porous and Rough Electrodes," Advances in Electrochemistry and Electrochem. Eng. 6, 329-397 (1967).

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65. Keiser, H., Deccu, K.D., and Gutjahr, M.A., "Abschätzung Der Porenstruktur Poroser Elektroden Aus Impedanzmessungen (Estimation of Pore Structure of Porous Electrodes from Impedance Measurement)," *Electrochimica Acta*, 21, 539,543 (1976).

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3 Great Pasture Road
Danbury, CT 06813

A. CONTRACTOR INFORMATION (CONTRACTOR COMPLETES PART A. 1-5)

Determination of Optimum Electrolyte Composition

1. Document Title: for Molten Carbonate Fuel Cells

2. Type of Document: ☒ Quarterly
☒ Technical Report. ☐ Technical Paper. ☐ Journal Article. ☐ Abstract.
☐ Conference Presentation. ☐ Other (please specify):

3. In order to meet a publication schedule or submission deadline, patent clearance by October 1987 is desired.
(date)

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☐ b. describes a possible Subject Invention relating to _____

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ii. A disclosure of the invention was submitted on _____

iii. A disclosure of the invention will be submitted by _____

iv. A waiver of DOE's patent rights to the contractor: ☐ has been granted.
☐ has been applied for; or ☐ will be applied for by _____

(date)

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Signed

A. Pigeaud
A. Pigeaud (contractor)

Date

7/1/87

Position Program Manager

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