SIMULATED COAL-GAS-FUELED MOLTEN CARBONATE FUEL CELL DEVELOPMENT PROGRAM

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Topical Report: Cathode Compatibility Tests

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TABLE OF CONTENTS

Section	Page
INTRODUCTION	1
CATHODE COMPATIBILITY TESTS	2
Objective	2
Conclusions	2
Summary	2
Background	4
Foreword and Report Organization	6
Report of Work	6
Cathode Materials	6
Test Rig	7
iR Compensation	12
Performance of Nickel Oxide	14
Performance of Alternate Cathodes	16
Crystallography	23
B.E.T. Surface Area And Scanning Electron Microscopy	24
Post-Test Microprobe Analyses	30
Electronic Conductivities Of Alternate Cathodes	34
Discussion	38
Recommendations	40
APPENDIX	A-1

LIST OF FIGURES

Figure	Page
1. Predictions of the IFC Cathode Performance Model	5
2. Schematic Of Corrosion Test Rig	8
3. Cathode Corrosion Rig 2 Prior to Testing	9
4a. Corrosion Rig 2 Pre-Test	11
4b. Corrosion Rig 2 Post-Test	11
5. AC Impedance Spectroscopy for iR Correction under ROX-3 at 650°F	12
6. iR from AC Impedance vs Time	13
7. Polarization Curves RIG1 on ROX-3	15
8. Polarization Curves RIG1 on MCO-D	16
9a. Polarization Curves for Nb: CeO ₂ under ROX-3	17
9b. Tafel Plots for Nb: CeO ₂ under ROX-3	17
10a. Polarization Curves for Nb: CeO ₂ under MCO-D	18
10b. Tafel Plots for Nb: CeO ₂ under MCO-D	18
11. Variation of Effective Exchange Current with Time for Niobium – Doped Ceria	20
12. Polarization Curves for Mg: Li ₂ MnO ₃ under ROX-3	21
13. Polarization Curves for Co: LiFeO ₂ under ROX-3	21
14. Polarization Curves for Ca,X: YIG under ROX-3	22
15. SEM of Nb: CeO ₂	26
16. SEM of Mg: Li ₂ MnO ₃	27
17. SEM of Co: LiFeO ₂	28
18. SEM of YIG	29
19. Electron Microprobe Analysis of the Ceria Cell Package	31
20. Microprobe Analysis of the Lithium Manganite Cell Package	33
21. Electronic Conductivity of Nb Doped Ceria in Dry ROX-3	36
22. Electronic Conductivity of Mg Doped Li ₂ MnO ₃ in Dry ROX-3	36
23. Electronic Conductivity of Co Doped Lithium Ferrite in Dry ROX-3	37
24. Electronic Conductivity of Doubly Doped YIG in Dry ROX-3	37

LIST OF TABLES

Table	Page
1. Pre-Test Physical Characteristics of Cathodes	7
2. Humidified Gas Compositions	10
3. Fill Levels for Corrosion Rigs	14
4. Polarization of Nickel Oxide Cathodes	16
5. Comparison of Exchange Current from Tafel Plots and Initial Slopes of Polarization for Nb: CeO ₂	19
6. Initial Slope of Polarizations at 100 mA/cm ²	22
7. Crystallography of Cathodes	23
8. B.E.T. Surface Area (m ² /g) of Cathodes	24
9. Conductivities (S/cm) of Alternate Cathode Materials at 650°C	35

INTRODUCTION

This work was conducted as part of DOE Contract DE-AC21-91MC27393. Results were reported in separate quarterly reports under Subtask 5.3 as specified by the contract.

In previous work, International Fuel Cells Corporation (IFC) found interactions between molten carbonate fuel cell cathode materials being considered as replacements for the presently used nickel oxide and matrix materials. Consequently, this work was conducted to screen additional new materials for mutual compatibility. As part of this program, experiments were performed to examine the compatibility of several candidate, alternative cathode materials with the standard lithium aluminate matrix material in the presence of electrolyte at cell potentials. Initial cathode candidates were materials lithium ferrite, yttrium iron garnet, lithium manganite and doped ceria which were developed by universities, national laboratories, or contractors to DOE, EPRI, or GRI. These investigations were conducted in laboratory scale experiments.

CATHODE COMPATIBILITY TESTS

OBJECTIVE

The objective of this task was to determine the compatibility of several candidate alternative cathode materials with lithium aluminate matrices in the cathode operating environment of pressurized fuel cells.

CONCLUSIONS

None of the materials tested can directly replace nickel oxide or indicate greater stability of cell performance than afforded by nickel oxide. Specifically:

- No further work on niobium doped ceria is warranted.
- Cobalt migration was found in the lithium ferrite cathode tested. This could possibly lead to shorting problems similar to those encountered with nickel oxide.
- Possible shorting problems may also exist with the proprietary dopant in YIG.
- Lithium ferrite and YIG cathode were not single phase materials. Assessment of the chemical stability, i.e., dopant loss, was severely impeded by dissolution of these second phases in the electrolyte.
- Magnesium doped lithium manganite warrants further work. Electrolytes should contain Mg ions to suppress dopant loss.

SUMMARY

Alternate materials were supplied by several laboratories throughout the country:

- Cobalt doped lithium ferrite (Argonne National Laboratory)
- Magnesium doped lithium manganite (Argonne National Laboratory)
- Niobium doped ceria (Case Western Reserve University)
- Calcium doped yttrium iron garnet (YIG), also containing a proprietary dopant (Ceramatec)

The test rig for evaluating compatibility was verified with nickel oxide cathode trials.

- Cathode performance data was obtained and showed good reproducibility.
- Data indicated gas diffusion polarization on diluted oxidant due to gas flow in the multi-station rig.
- Polarizations were consistent with the IFC cathode performance model obtained on rich oxidant.
- Values for surface area and performance were consistent with typical IFC cathodes.

Results for alternate materials noting changes during corrosion testing:

Niobium doped Ceria

- Phase, grain size and surface area stable

- Niobium loss correlated to oxygen partial pressure
- Poor catalytic performance
- Order of magnitude decrease in conductivity after testing

Magnesium doped Lithium Manganite

- Multi crystal phase sample, small amount of interconversion after testing
- Grain size decrease, 3X surface area increase after testing
- Performance relatively constant
- Mn migration during test
- Order of magnitude decrease in electronic conductivity

Cobalt doped Lithium Ferrite

- Multiple chemical phases after testing
- Second phases leached during test, pure phase after testing
- Order of magnitude increase in grain size
- Performance increases over the course of the test
- Co and Fe migration during test
- Over two orders of magnitude increase in conductivity after testing

Calcium and proprietary doped Yttrium Iron Garnet

- Initial phase identified as cubic YFeO_3 instead of the CERAMATEC assignment as garnet, $\text{Y}_3\text{Fe}_5\text{O}_{12}$. Excess iron occurs as Fe_3O_4 and spinel containing proprietary dopant.
- Sample multi-phase post-test, some second phase leached by electrolyte, primary phase stable
- Slight grain size increase, surface area stable
- Performance increases then slightly decreases from maximum
- Fe and proprietary dopant migration during test
- Electronic conductivity decreases a factor of 20 during testing

Performance data was only able to identify ceria as a much poorer catalyst than nickel oxide, exchange currents were over four orders of magnitude lower.

BACKGROUND

Lithiated nickel oxide cathodes that are presently used in molten carbonate fuel cells are both performance and life limiting. The cathode is a major source of cell polarization and cathode dissolution is a serious decay mode. This dissolution can be reduced to an acceptable level by changing the cell design and operating the cell at conditions which reduce its performance. For example, the dissolution rate can be lowered by decreasing the carbon dioxide pressure at the cathode; however, the cell voltage is concomitantly lowered. The cathode is also fragile from a physical standpoint. These features result in a complex optimization of the cathode configuration.

Nickel oxide dissolution results in the deposition of metallic nickel in the matrix.¹ This nickel deposition can cause the formation of electronically conducting bridges between the electrodes which degrade cell performance. Structural deterioration of the cathodes can also occur due to loss of material. Since this dissolution is potentially one of the most severe modes of performance decay, alternate materials with greater stability have been sought.

Desirable properties of a nickel oxide replacement material have been identified and are listed below. Properties 1 to 5 address the stability of the cathode while properties 6 to 10 refer to performance.

1. Solubility as anion mole fraction less than 10^{-5} at 1300°F for 1 atm to 10 atm total pressure (carbon dioxide pressure max = 2 atm).
2. Solubility as cation less than 2×10^{-6} mole fraction. At the same conditions as 1.
3. Soluble species must not be reduced to a metal or oxide with lower solubility at the anode.
4. Crush strength of the porous electrode at 1300°F greater than 50 psi.
5. Creep or compaction less than 1 mil at 1300°F.
6. Electronic conductivity greater than 0.5 S/cm as a compacted solid in the cathode environment.
7. Must be able to be fabricated into a porous cathode with greater than 70 percent porosity.
8. Mean pore diameter of 5μ .
9. Pore spectrum must have 20 percent of the porosity in pores less than 1μ in diameter.
10. High catalyst activity for electron transfer reactions.

Candidates have been uncovered for use as replacements for nickel oxide that demonstrate low solubilities but have electronic conductivities lower than desired. An IFC cathode performance model^{2,3} was therefore used to predict cathode overpotential in millivolts versus electronic conductivity in S/cm as shown in Figure 1. The cathodic reaction on the alternate materials was assumed to be as fast as on nickel oxide. The model predicts that because the alternate materials have a lower electronic conduc-

¹W.M. Vogel, L.J. Bregoli, H.R. Kunz and S.W. Smith, "Stability of NiO Cathodes in Molten Carbonate Fuel Cells," The Electrochem. Soc. Proc. 84-13, 443 451 (1984).

²H.R. Kunz, L.J. Bregoli, and S.T. Szymanski, "A Homogeneous/Agglomerate Model for Molten Carbonate Fuel Cell Cathodes," J. Electrochem Soc., vol 131 p2815 (1984).

³H.R. Kunz and L.A. Murphy, "The Effect of Oxidant Composition on the Performance of Molten Carbonate Fuel Cells," J. Electrochem. Soc., vol 135 p1124 (1988).

tivity than nickel oxide a higher polarization will be observed. Some of this polarization can be recovered by decreasing the porosity and the electrode thickness based on IFC power plant system studies. This polarization is projected to be more than compensated by the ability of the cell to run at higher pressure and cathode carbon dioxide contents than NiO cells of comparable life, resulting in improved power plant performance. Note that the electronic conductivity abscissa in Figure 1 is that of the solid cathode material corrected for porosity.

The leading candidates (identified as potentially meeting the above criteria) are the subjects of the present investigation: (niobium) doped ceria, (cobalt) lithium ferrite, (magnesium) lithium manganite, and doped yttrium iron garnet. The conductivity values of these materials are marked by arrows in Figure 1. Though alternate materials exhibit lower electronic conductivities than nickel oxide, the IFC theoretical studies show that the cost per kW of a 40,000 hour lifetime power plant could be less for these materials than for nickel oxide. Therefore, the electronic conductivities of these materials may be acceptable, however, other properties must be evaluated. In the present study, the corrosive interactions among the cathode, electrolyte, and matrix material are investigated under the complete cathode environment.

*This work

+J.L. Smith, G.H. Kucera, and A.P. Brown "Development of Cathode Material and Structures for the Molten Carbonate Fuel Cell", Proceeding of the Second Symposium on Molten Carbonate Fuel Cell Technology, Volume 90-16, P 226 (1990).

Figure 1. Predictions of the IFC Cathode Performance Model

FOREWORD AND REPORT ORGANIZATION

The purpose of this investigation is to assess the stability of alternate cathode materials in the complete cathode environment of a molten carbonate fuel cell. Cathodes have been characterized before (pre-test) and after (post-test) being subjected to cathodic environments for approximately 1500 hours. Cathodic environment refers to contact with lithium aluminate, molten lithium/potassium carbonate, and stainless steels at 650°C in an oxidizing atmosphere under an electrical potential.

In this work, pre-test and/or post-test cathodes were characterized by: x-ray diffraction crystallography, mercury intrusion porosimetry, B.E.T. surface area, scanning electron microscopy, electron microprobe analyses, or electrical conductivity measurements.

The corrosion testing actually took place in an electrochemical half cell so that performance data could be obtained. Cathode structures have not been optimized for performance, so direct comparisons with nickel oxide are difficult, however, changes in electrochemical characteristics with time in the cathodic environment are meaningful.

This report is organized into sections as follows: A description of cathode formation, materials, and properties is followed by a description of the electrochemical test vehicle and procedure. The performance data of the cathodes are compared to nickel oxide and changes over time noted. Characterization of the cathodes is compared pre-test and post-test and a judgement of stability is made.

REPORT OF WORK

Cathode Materials – Cathode materials have been supplied by institutions in the United States: cobalt doped lithium ferrite and magnesium doped lithium manganite cathodes from Dr. G. Kucera at Argonne National Laboratory (ANL), cathodes of doped yttrium iron garnet (YIG) from Dr. S. Elangovan at Ceramtec, and niobium doped ceria powder from Prof. M. DeGuire at Case Western Reserve University (CWRU).

Chemically prepared one mole percent niobium doped ceria powder from CWRU was formed into cathodes at IFC. The powder was milled for one hour, dispersed in a hydrocarbon solvent, binder added, and cast into a tape. The 0.0178 cm tape was cut into 2.42 cms discs, four discs were laminated and fired at 1400°C for two hours in air. These discs were used in subsequent experiments.

Lithium manganite was received as thin discs approximately 2.54 cms diameter and 0.023 cms thick. The discs were pre-sintered at ANL at 1175°C and were back filled with binder for mechanical strength. Two discs were used in the corrosion test and delaminated after testing. ANL requested that no judgements be made on the absolute electrochemical performance of this material.

Lithium ferrite was received as a tape cast layer 0.030 cms thick. This layer was cut into discs 2.22 cms in diameter. Two discs were used for corrosion testing and remained laminated post-test. Lithium ferrite underwent a small amount of sintering at 650°C.

Doped YIG was received as pre-sintered discs and used without further treatment. YIG is doped with calcium and a proprietary dopant referred to as X in this report.

Table 1 shows the pre-test physical parameters for the cathodes in this study. Equivalent post-test measurements were impossible because of physical damage to the cathodes during teardown.

Table 1. Pre-Test Physical Characteristics of Cathodes

Cathode	% Theoretical Density*	Median Pore Diameter (μ)	Diameter (cm)	Thickness (cm)	Mass (g)
Nb:CeO ₂	54	2.14	2.42	0.0767	1.3814
Mg:Li ₂ MnO ₃	46	3.51	2.66	0.0479	0.4796
Co:LiFeO ₂	29	2.02	2.22	0.0543	0.2654
Ca, X:YIG	53	1.39	1.89	0.0747	0.5642
Li:NiO ⁺	39	3.69	2.42	0.0495	0.5313

**Based on geometric densities and theoretical densities of 7.212, 3.90, 4.42 and 5.10 g/cc, respectively; NiO based on porosimetry
+ Cathode No. 1 of first corrosion rig.*

Test Rig – The cathode corrosion rig is shown schematically in Figure 2. Electrochemical half cells are formed in this rig with each of the “cathode(s) under test” serving as the working electrodes. The central position of (Li) NiO is the reference electrode while the bottom large layer of (Li) NiO serves as the counter electrode. The section of the counter electrode directly under the reference was removed and replaced with an alumina disc of the same thickness. The matrix of lithium aluminate is formed from three plies of 0.0229 cm thick tape and is 100 percent filled with an electrolyte of 62 mole % lithium carbonate and 38 mole percent potassium carbonate. The rig used in all experiments has four test stations, i.e., four working electrodes. The outer envelope, top flange, inside structural parts and current collectors were fabricated from 316 stainless steel.

The electronics allowed application of the same potential to all four working electrodes simultaneously while current could be measured individually.

A 40 psi load was applied to the cell packages by spring loading the alumina tubes as shown in Figure 3. The figure also gives a good view of the configuration of the apparatus.

Three gas compositions were used for corrosion and performance testing, humidified ROX-3, MCO-D, and Sim-Mix. Molar compositions are shown in Table 2. The Sim-Mix composition simulates at one atmosphere total pressure oxygen and carbon dioxide partial pressures that a cathode would encounter under operation of a fuel cell at 60 psia. Total flow rate was generally between 120 and 150 SCCM.

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Figure 2. Schematic Of Corrosion Test Rig

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Figure 3. Cathode Corrosion Rig 2 Prior to Testing

Table 2. Humidified Gas Compositions

Gas	Mole % O ₂	Mole % CO ₂	Mole % H ₂ O	Mole % N ₂
ROX-3	9.5	7.2	18.7	64.6
MCO-D	27.1	54.2	18.7	—
Sim-Mix	38.0	28.8	33.2	—

Two corrosion experiments were run sequentially in the same apparatus. The first experiment, Rig 1, ran for 320 hours under ROX-3 with four lithiated nickel oxide working electrodes. This rig served to check out the hardware and electronics and obtain baseline data on nickel oxide. The second experiment, Rig 2, ran for 1500 hours, 309 under ROX-3 and 1191 under Sim-Mix, with four alternate materials as the working electrodes.

In both cases, the working electrodes were potentiostated at 40 millivolts below the reference electrode while measuring performance. The electrolyte potential will shift with gas composition. This shift is automatically compensated by simulating the potential of a cathode in an operating fuel cell as 40 mV below the open circuit potential.

All NiO electrodes were formed by in-situ oxidation of porous nickel electrodes. Oxidation is performed under ROX-3 diluted 1 to 4 with nitrogen at approximately 480°C. A high degree of buckling in the unconstrained areas of the large counter electrode was found post-test in Rig 1, presumably due to the volume expansion of the nickel to nickel oxide conversion. The matrix over the buckled area was cracked, but electrical measurements indicate that ionic contact was maintained. Therefore, in Rig 2, the counter electrode was pre-oxidized while constrained over the total area before mounting in the corrosion rig. Figure 4a, Rig 2 pre-test, and Figure 4b, Rig 2 post-test, show that this pre-oxidation was ineffective in preventing the buckling. Surprisingly, low iR 's can be obtained with this amount of buckling.

Figure 4a. Corrosion Rig 2 Pre-Test

Figure 4b. Corrosion Rig 2 Post-Test

iR Compensation – Experimental polarizations were corrected for internal cell resistance (iR). Cell resistances (R) were measured by ac impedance spectroscopy. Figure 5a shows a typical graphical output of this analysis for nickel oxide. The plot of the imaginary part of the impedance $\text{Im}(Z)$ vs. the real part of Z crosses the $\text{Im}(Z) = 0$ axis at the cell resistance. After correcting for the resistance of the electrical leads, the average cathode half cell resistance is obtained. The experimental polarization is corrected by subtracting the product of the total cell current times the cathode half cell resistance from the measured polarization and is reported as the iR free polarization. Therefore, a cell resistance measurement must be performed for each cathode under each gas for each polarization curve. Corrections for cathodes of alternate materials was not as straightforward as those for nickel oxide. The curve in Figure 5b. was extrapolated to cross this axis.

Figure 5. AC Impedance Spectroscopy for iR Correction under ROX-3 at 650°F

AC impedance plots for lithium ferrite and YIG closely resemble those for nickel oxide at all times and atmospheres. Plots for lithium manganite appear distorted by extension of the curve in the negative $\text{Im}(Z)$ quadrant while those of ceria are quite different and do not cross the $\text{Im}(Z) = 0$ axis.

Measured cell resistances contain contributions from resistance of the electrical leads, contact resistance of the current collector and cathode, ionic resistance of the electrolyte in the matrix, and resistance of the cathode material. Contributions from the anode side are neglected. The first three of these effects combine in a simple series sense. The resistance of cathode material, however, acts through a complex combination of series and parallel circuits made by electronic, ionic, and electrochemical paths in the porous cathode.

For a first approximation, the electronic resistivity of the cathode material can be neglected when it is much smaller than the resistivity of the electrolyte in the matrix. When the resistance of the cathode becomes large compared to the resistance of the electrolyte, the plot of the real vs. imaginary part of the impedance changes from that of a resistor, (a vertical line in the $+\text{Im}(Z)$ quadrant), to that of a resistor-capacitor parallel combination (part of a semicircle in the $-\text{Im}(Z)$ quadrant). The cell resistance, taken as an extrapolation of the high frequency end of the arc, then reflects the resistivity of the cathode. Figure 5b shows precisely this scenario for ceria. Further analyses are possible with ac impedance spectroscopy, but beyond the scope of this work.

Figure 6 tracks the increase in measured cell resistance with time and gas composition. A logarithmic ordinate simplifies presentation. Measurements start at 46 hours under ROX-3. Initial differences in the cell resistances may reflect contact resistance though this was neglected in further analyses. At 200 hours, measurements are taken in both ROX-3 and MCO-D and show little dependence. After 300 hours, the measurements were taken with all three gases. Ceria shows a large increase in resistance after switching to the Sim-Mix gas. Manganite shows a much smaller increase while YIG and lithium ferrite are nearly unaffected.

12292-52
922204

Figure 6. iR from AC Impedance vs Time

The cell resistance of ceria not only increases by an order of magnitude after switching to the Sim-Mix soak gas, but also changes with measurement atmosphere. The dependence of the cell resistance on gas composition at about 550 hours for ceria does not correlate with oxygen pressure. DeGuire et.al.,⁴ found that the resistance of ceria increases with increasing oxygen pressure in this pressure range. However, this dependence on atmosphere disappears at 1500 hours. The large increase in cell resistance is used to interpret the post-test electronic conductivity of ceria reported later.

The small increase in cell resistance between 550 and 1500 hours observed in all cells can be attributed to electrolyte loss. Table 3 shows that post-test electrolyte fill levels of Rig 2 are much lower than expected, even for the matrix. In Rig 1 the electrolyte was maintained at 100 percent in the matrix after 320 hours of operation.

⁴M. R. DeGuire, M. J. Singler, and E. Dincer, "Doped Cerium Oxide for Molten Carbonate Fuel Cell Cathodes," Case Western Reserve University, EPRI ER-6983, Final Report Project 2278-6, Sept. 1990, p3-9.

Measured polarizations for alternate materials contain contributions from the electronic resistivity of the cathode. This resistance is inherent in the materials, and to correct for this loss would bias the data in favor of smaller polarization losses which could not be realized. Therefore, all measured polarizations were corrected using the measured cell resistance for lithium ferrite since this was the closest to nickel oxide. This way, polarizations are corrected for changes in the resistivity of the electrolyte in the matrix due to fill level and gas composition.

Table 3. Fill Levels for Corrosion Rigs

Body	Calculated* Pre-Test Fill (%)	Measured Post-Test Fill (%)
Rig 1		
NiO	40	5 samples 23, 25, 26, 26, 30
Matrix	100	4 areas 92, 95, 98, 105
Rig 2		
Nb:CeO ₂	70	25
Mg:Li ₂ MnO ₃	52	32
Co:LiFeO ₂	74	—
Ca,X:YIG	85	29
Matrix	100	77
<i>*Based on an equivalent pore diameter of 3.8μ for NiO at 40% fill.</i>		

Performance of Nickel Oxide – The test rig was run with four nickel oxide-cathodes as the working electrodes to check the facility. All electrodes were in situ oxidized and filled with electrolyte to nominally 40 percent of their pore volume. Performance was measured under humidified ROX-3 and MCO-D. The rig and electronics resulted in the performance data shown in Figures 7 and 8. The figures illustrate the iR free polarizations of the four nickel oxide cathodes vs. current density under ROX-3 and MCO-D, respectively. Each figure exhibits the reproducibility among the four cathodes and shows curvature at higher current densities.

The higher polarization observed under ROX-3 compared to MCO-D is consistent with gas phase diffusion polarization. Insets to the figures give the individual cathode polarization at 100 ma/cm². The average values are presented in Table 4 at different times and at gas compositions where deviations represent one standard deviation. Calculated values of anticipated polarization based on the IFC cathode computation model are also listed in the table. The difference in experimental versus calculated is attributed to gas phase polarization.

The measured polarizations on ROX-3 shown in Figure 7 can be seen to be within a narrow band for the four working electrodes, but 50 to 60 mV above the anticipated level as shown in Table 4. The polarization decrease from 72 to 285 hours under ROX-3 is likely an artifact due to iR compensation measured under MCO-D used to compensate measurements under ROX-3. In further experiments,

iR compensation was measured under the same atmosphere as the polarization. The post-test fill levels of the cathodes and reference are given in Table 3.

Gas flow was increased to try to reduce the gas phase polarization. However, a variation of the gas flow from 80 to 240 SCCM into the corrosion rig did not alter this polarization. Actual stack hardware was used in the cathode corrosion rig to simulate the complete cathode environment in a stack since the primary objective of this program is to evaluate corrosion stability of the cathode materials. These stack hardware components are thought to result in the gas diffusion polarization in the half-cell configuration of the corrosion rig. Specifically the thick pressure plates, Figure 3, block gas flow to the cathodes. Nevertheless, relative cathode performances can be obtained for the various materials with both ROX-3 and MCO-D as reactants.

12292-05
922204

Figure 7. Polarization Curves RIG1 on ROX-3

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922204

Figure 8. Polarization Curves RIG1 on MCO-D

Table 4. Polarization of Nickel Oxide Cathodes

Hot Time (Hours)	Atmosphere	IR-Free Polarization mV at 100 ma/cm ²	Calc. Pol. mV	Cell* Resistance (Ω)	Atmos. for Resist. Meas.
72	ROX-3	93 ± 7	33	0.111	ROX-3
285	ROX-3	83 ± 1	33	0.082	MCO-D
288	MCO-D	19 ± 3	30	0.082	MCO-D
318	MCO-D	21 ± 3	30	0.082	MCO-D

*Measured by ac impedance (note 100 ma/cm² = 92.9 ASF)

Performance of Alternate Cathodes – Polarization curves and associated Tafel plots were obtained for each cathode under each gas: ROX-3, MCO-D, and Sim-Mix. Those curves are provided in the Appendix.

The polarization curves for niobium doped ceria measured at various times under ROX-3 are shown in Figure 9a. The polarizations are much higher than those observed for nickel oxide and show sections which appear to be kinetically controlled. The Tafel plots in Figure 9b, show straight sections with slopes around 400 mV/decade ($2RT/F = 366$ mV/decade at 650°C). The polarizations form two groups which correlate with the start of the Sim-Mix soak gas and are independent of time. Figures 10a and 10b for this cathode under MCO-D show similar behavior.

12292-37
922204

Figure 9a. Polarization Curves for Nb: CeO₂ under ROX-3

12292-38
922204

Figure 9b. Tafel Plots for Nb: CeO₂ under ROX-3

12292-54
922204

Figure 10a. Polarization Curves for Nb: CeO₂ under MCO-D

12292-55
922204

Figure 10b. Tafel Plots for Nb: CeO₂ under MCO-D

Comparison of exchange currents, i_0 , derived from extrapolation of Tafel plots, Figures 9b and 10b, and the initial slope of the polarization curves, Figures 9a and 10a, is shown in Table 5. The exchange current is related to the initial slope by:

$$i_0 = \frac{RT}{F} \times (795 \text{ mV}) \times \frac{1}{\text{Slope}} \times \frac{\text{Frontal area}}{\text{Total area}}$$

The agreement is excellent indicating electron transfer limitation of the current at current densities up to approximately 3 mA/cm². In this case, the measured exchange current can be directly compared to that for nickel oxide, 5 x 10⁻⁴ mA/cm² vs. 20 mA/cm², respectively⁵. Clearly, niobium doped ceria is a much poorer catalyst than nickel oxide.

Table 5. Comparison of Exchange Current from Tafel Plots and Initial Slopes of Polarization for Nb: CeO₂		
	Exchange Current (i_0) (mA/cm²)*	
Time (h)	Tafel (10⁻⁴)	Initial Slope (10⁻⁴)
Measured under ROX-3		
42	5.0	4.5
215	5.0	4.7
545	2.3	1.8
1506	2.3	2.0
Measured under MCO-D		
210	5.0	5.3
530	2.0	1.7
1508	2.0	1.7
Measured under Sim-Mix		
527	1.7	1.05
1486	2.7	1.6
<i>*Currents are value x10⁻⁴ mA/cm² of real surface area 2.76 x 10³ cm²</i>		

⁵I. Uchida, Y. Mugikura, T. Nishina and K. Itaya, "Gas Phase Reactions in Molten Carbonate Media, Part II. Oxygen Reduction Kinetics on Conductive Oxide Electrodes in (Li + K) Eutectic at 650°C," J. Electroanal. Chem. **206** 241-252 (1986).

Figure 11 is a plot of the exchange current derived from the initial slopes of the polarization curves versus time for ceria. This figure clearly demonstrates the dependence on soaking gas rather than time. The ceria cathode undergoes a change which reduces its catalytic properties.

12292-39
922204

Figure 11. Variation of Effective Exchange Current with Time for Niobium - Doped Ceria

Polarization curves for the other cathodes under ROX-3 are shown in Figures 12 to 14. None of these cathodes show an identifiable Tafel region (See Appendix). Polarization of lithium manganite decreases with time except at 1506 hours. This final increase is most likely due to the increased cell resistance. The trend is also mirrored in the polarization curves for YIG, though the polarizations are much smaller in this case. The polarization of lithium ferrite simply decreases with time.

Lack of a Tafel region implies that electron transfer at the cathode surface is not the rate limiting step. Therefore, the polarization curves for manganite, ferrite and YIG do not yield information concerning the catalytic properties of these cathodes and rather reflects changes in conductivity and diffusional and gas phase losses.

The IFC cathode performance model was used to predict polarizations at 100 mA/cm² for NiO under ROX-3, Table 4. Extrapolating polarizations at low current densities to 100 mA/cm² for the alternate materials gave polarizations much higher than those predicted by this model. Extrapolated values and model predictions are given in Table 6. Polarizations for lithium ferrite and YIG are only a factor of 5 and 3 above that predicted by the model. This is acceptable given the approximations of the model and the effects of gas phase polarization due to the half-cell hardware. Therefore, the IFC model reasonably describes the polarization of these cathodes. The IFC model assumes that surface electron transfer reactions are very fast compared with other sources of polarization. Lack of a Tafel slope and reasonable agreement with the IFC Cathode Performance Model both indicate electron transfer is not limiting the behavior of lithium ferrite and YIG.

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Figure 12. Polarization Curves for Mg: Li_2MnO_3 under ROX-3

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Figure 13. Polarization Curves for Co: LiFeO_2 under ROX-3

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Figure 14. Polarization Curves for Ca,X: YIG under ROX-3

Table 6. Initial Slope of Polarizations at 100 mA/cm ²			
	Polarization (mV)		
Time (h)	Mg: Li ₂ MnO ₃	Co: LiFeO ₂	Ca, X: YIG
Measured under ROX-3			
42	6400	1400	940
215	3500	990	386
545	2200	596	233
1506	2700	335	268
IFC Cath Performance Model	> 160	60	89
Measured under MCO-D			
210	2700	1700	512
550	2100	920	170
1508	2500	155	287
Measured under Sim-Mix			
527	2100	670	224
1486	2500	228	224
Notes:			
1) All samples soaked at -40 mV relative to NiO in soaking atmosphere			
2) Soaking atmosphere ROX-3 0-309 hours; Sim-Mix 309-1508 hours			
3) NiO under ROX-3; 71 mV MCO-D ~ 11 mV at ~ 300 hours			

Crystallography – Pre-test and post-test cathode materials were examined by XRD to determine the phases present. Results are summarized in Table 7. Pre-test samples of Nb:CeO₂ and YIG were examined without further treatment while those of LiFeO₂ and Li₂MnO₃ were given a heat treatment at 650°C in air to remove binder. Post-test samples were examined without carbonate removal to assure that soluble phases were not removed. Interference of carbonate in the XRD data was minimal due to scrupulously eliminating contact with water vapor.

Table 7. Crystallography of Cathodes

Cathode Material	Phases Pre-Test*	Phases Post-Test
Nb:CeO ₂	Single Phase fcc CeO ₂	~ 97-99 v/o fcc CeO ₂ ~ 3-1 v/o mono Nb ₂ O ₅
Mg:Li ₂ MnO ₃	~ 65-70 v/o fcc mono Li ₂ MnO ₃ ~ 25-20 v/o spinel LiMn ₂ O ₄ ~ 10-5 v/o mono and fcc ZrO ₂ possible ~ 1 v/o ortho LiMnO ₄	~ 35-40 v/o mono Li ₂ MnO ₃ ~ 55-50 v/o fcc spinel LiMn ₂ O ₄ ~ 10-5 v/o mono and fcc ZrO ₂
Co:LiFeO ₂	~ 90 v/o fcc LiFeO ₂ ~ 10 v/o hex Li CoO ₂	Single Phase fcc + α - LiFeO ₂
YIG	~ 75-70 v/o ortho FeYO ₃ ~ 25-30 v/o fcc spinel Fe ₃ O ₄ and/or X Fe ₂ O ₄	~ 80-75 v/o ortho FeYO ₃ ~ 20-25 v/o fcc spinel Fe ₃ O ₄ and/or X Fe ₂ O ₄
*fcc = face centered cubic mono = monoclinic ortho = orthorhombic hex = hexagonal X = proprietary dopant of YIG + one strong and four weak reflections unaccounted for		

Niobium doped ceria loses niobium oxide while at temperature. The loss may be correlated with atmosphere as previously discussed. The initial concentration of Nb, 1 mole percent, is near the solubility limit at 1600°C and solubility decreases with temperature.⁶ Obviously the solubility limit was exceeded at 650°C. The exsolved niobium oxide does not dissolve in molten carbonate nor react to form lithium niobate. The second phase thus produced may inhibit conductivity at the grain boundaries, a decrease in conductivity post-test is observed. Notably absent are Ce₆O₁₁, Ce₁₁O₂₀, and CeNbO₄ phases found by DeGuire et. al.⁶ after testing in molten carbonate.

Lithium ferrite contains a large amount of lithium cobaltite, presumably excess initial dopant. Many workers find lithium cobaltite soluble in molten carbonate. The absence of this phase post-test supports the high solubility of cobaltite in molten carbonate. Increase of the conductivity post-test implies that some of the initial excess cobalt present migrated into the lithium ferrite.

⁶DeGuire, Shingler & Dincer, op.cit. pp 4-3 - 4-13

Magnesium doped lithium manganite contains both monoclinic and spinel phases. The zirconia phase, presumably is present from processing with zirconia grinding media. Enrichment in the spinel phase occurs post-test and may affect the surface area change and microstructure changes during testing.

The assignments for doped YIG do not concur with CERAMTEC⁷. Samples prepared with the garnet formula $Y_3Fe_5O_{12}$ would yield excess iron if the present assignment is correct. This assignment is thus supported by the presence of the spinel iron oxide. Distribution of the dopant in a second phase is possible. Interestingly, the orthorhombic phase is stable at temperature. Loss of the proprietary dopant, X, as well as the Ca, is possible. These dopants are soluble in molten carbonate.

In summary of XRD determinations, lithium ferrite and YIG appear phase stable in the cathode environment. Niobium doped ceria loses niobium while lithium manganite shows a gradual conversion from the monoclinic to the spinel phase in the cathode environment.

B.E.T. Surface Area and Scanning Electron Microscopy – B.E.T. surface areas and Scanning Electron Microscopy (SEM) were performed on pre-test and post-test cathode materials. Pre-test analyses were performed on similar samples to those corrosion tested. Lithium ferrite and lithium manganite were given a heat treatment cycle at 650°C to simulate binder removal and sintering in a cell startup. This was not necessary for ceria and YIG since they were already processed at higher temperatures. Post-test analyses were performed on actual test samples after electrolyte removal with acetic acid-acetic anhydride.

Surface areas in Table 8 show relative stability for ceria and YIG. Lithium manganite increases by a factor of three. The surface area of nickel oxide from the first corrosion rig which operated for 300 hours is given for reference.

Table 8. B.E.T. Surface Area (m²/g) of Cathodes

Cathode Material	Pre-Test*	Post-Test
Nb:CeO ₂	0.15	0.24
Mg:Li ₂ MnO ₃	0.46	1.26
Co:LiFeO ₂	2.19	— ⁺
YIG	0.22	0.19
NiO	—	2.15

*average of two determinations, difference as percent of average were 19, 2, 25, and 14, respectively
⁺lithium ferrite crumbled post-test - unable to distinguish from NiO

⁷B. K. Rolfson, S. Elangovan, and A.C. Kandkar, "Alternative Cathodes for Molten Carbonate Fuel Cells," Ceramtec, Inc., EPRI ER/GS-6831, Final Report Project 2278-1, May 1990, p 4-5.

The lithium ferrite cell package, ferrite-matrix-nickel oxide, crumbled after testing. The lithium ferrite was visually indistinguishable from nickel oxide so no surface areas could be obtained. A factor of five to ten decrease in surface area can be estimated from the SEM pictures described below.

The consistency of the surface area for YIG and ceria may result from the crystal phase stability and low solubility in the electrolyte. The increase of area for lithium manganite may be due to the phase changes in this material, the volume mismatch among phases may cause crystal strain which is relieved by decreasing particle size. Lithium ferrite, though phase stable, shows a ripening of the crystal size similar to nickel oxide. This may indicate a solution-precipitation mechanism. However, lithium ferrite has a considerable ionic mobility at 650°C since sintering occurs at this temperature, and thermal ripening may occur. Measurements at temperature without electrolyte could distinguish between these mechanisms.

SEM micrographs are shown in Figures 15-18. Good correlation between the pre-test and post-test surface areas and microscopy exists.

Figure 15 shows pre-test and post-test micrographs at 500X and 2000X for niobium doped ceria. The major effects observed are slight grain growth and grain boundary development. Further grain growth may be limited due to the exsolution of the niobium dopant.

Lithium manganite surface area increase is evident from Figure 16. The grain growth apparent in the other cathode materials is absent, in fact, a grain size reduction occurs. This may be due to the gradual shift from the monoclinic to the spinel phases.

Lithium ferrite shown in Figure 17 exhibits a large amount of grain growth. Post-test, the grains are prismatic implying some type of deposition from solution. Therefore, increasing the initial surface area of a cathode with lithium ferrite would have little benefit to its long term performance.

Doped YIG shows minor grain growth in Figure 18. Amorphous looking granules apparent in the pre-test pictures crystallize with small grains and may explain why only a minor change in surface area is observed with a rather large increase in grain size.

500 x Pre-Test

500 x Post-Test

2000 x Pre-Test

2000 x Post-Test

12292-43
922204

Figure 15. SEM of Nb: CeO₂

500 x Pre-Test

500 x Post-Test

2000 x Pre-Test

2000 x Post-Test

12292-44
922204

Figure 16. SEM of Mg: Li_2MnO_3

500 x Pre-Test

500 x Post-Test

2000 x Pre-Test

2000 x Post-Test

12292-45
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Figure 17. SEM of Co: LiFeO₂

500 x Pre-Test

500 x Post-Test

2000 x Pre-Test

2000 x Post-Test

12292-47
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Figure 18. SEM of YIG

Post-test Microprobe Analyses – Qualitative elemental microprobe analyses indicate the solubility and migration of species. After corrosion testing, small pieces of cell packages, cathode/matrix/anode, were mounted in epoxy, polished in a hydrocarbon liquid, and examined in the electron microprobe without carbonate removal. Micrographs are reproduced in this section for illustrative purposes; not for complete documentation. The figures in this section show the electron back scattered image (normal SEM) at 100X followed by x-ray maps specific for a given element of the same area. The concentration of white dots in an x-ray map is proportional to the concentration of the element in that area multiplied by a sensitivity factor.

Figure 19b shows that the matrix is devoid of cerium and the cathode-matrix interface is sharp suggesting that ceria is insoluble in molten carbonate. However, a high concentration of nickel can be found in the matrix in Figure 19c, as expected from the high solubility. In this particular half cell, nickel oxide acts as the anode, therefore, the cell potential drives nickel ions into the matrix. Nickel actually migrates into the ceria cathode as shown in Figure 19c.

Figure 20b shows a high concentration of manganese in the matrix extending into the anode. Nickel migration continues throughout the matrix into the cathode as shown in Figure 20c. The occurrence of both nickel and manganese in the same areas of the matrix is not an artifact; there are no overlaps of the x-ray emissions of the two elements. The implied solubility of manganese in the electrolyte is at odds with the sharp delimitation between cathode and matrix. The three plies of the matrix can be seen in Figure 20a.

Lithium ferrite shows a low concentration of iron and nickel throughout the matrix. Nickel has migrated into the ferrite cathode while the iron has migrated into the nickel oxide anode. The cathode-matrix interface is less well defined than for ceria and lithium manganite. A layer high in iron appears in the matrix next to the cathode. These effects could be attributed to the relatively high solubility of the ferrite in molten carbonate and would be consistent with the large amount of grain growth observed in the SEM.

The cathode-matrix interface is less well defined for YIG than for ceria and lithium manganite as determined by iron maps. Iron is also found throughout the matrix. The source of this iron may be the second phase rather than YIG. Yttrium is not found in the matrix nor at the interface of the cathode and matrix. A diffuse layer high in the proprietary dopant appears in the matrix adjacent to the cathode. This picture is consistent with the continual leaching of the dopant from the YIG.

To compare alternate materials with baseline nickel oxide, the matrix adjacent to the nickel oxide reference electrode was also examined. The matrix contained no nickel and the electrode-matrix interface was sharp at 100X.

The microprobe analyses are consistent with the following conclusions: Ceria, niobium, and yttrium oxides are not soluble in molten carbonate. Manganese, iron, and nickel oxides are all somewhat soluble so migration of these elements occurs. Furthermore, the proprietary dopant from YIG can be found in a diffuse layer adjacent to the cathode in the matrix. The relative solubilities of these oxides to nickel oxide would appear to be appreciable since no nickel was found next to the NiO reference. For each cathode, the ion must migrate against the potential gradient to appear in the matrix. This potential gradient is absent in the reference electrode (counter electrode was removed under the reference) so nickel migration should have been more pronounced than in a fuel cell.

Figure 19a. Backscatter Image at 100X

Fig. 19b. Cerium Map of the Area in Fig. 19a

12292-48
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Figure 19. Electron Microprobe Analysis of the Ceria Cell Package

Fig. 19c. Ni Maps of the Area in Fig. 19a

12292-49
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Figure 19. Electron Microprobe Analysis of the Ceria Cell Package (Cont'd)

Fig. 20a. Backscatter Image at 100X

Fig. 20b. Mn Map of the Area in Fig. 20a

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Figure 20. Microprobe Analysis of the Lithium Manganite Cell Package

Fig. 20c. Ni Map of the Area in Figure 20a

12292-51
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Figure 20. Microprobe Analysis of the Lithium Manganite Cell Package (Cont'd)

Electronic Conductivities of Alternate Cathodes – Measurements of electronic conductivity on cathode materials was performed pre-test and post-test using a four point Van Der Pauw technique.⁸ Contact was made by pressing four spring loaded platinum wires against the sample and applying a small amount of Pt paste. Since the conductivity of some samples depends on oxygen and/or carbon dioxide pressure, these were kept constant and all measurements were made under dry ROX-3 (8.9m% carbon dioxide, 11.6m% oxygen, and 79.5m% nitrogen).

Pre-test measurements were made on samples identical to those used as cathodes. Lithium manganite and lithium ferrite were given a heat treatment at 650°C prior to mounting in the conductivity cell to remove binder and simulate any sintering which would occur during cell start-up.

Post-test measurements were performed on broken pieces of cathodes which contained carbonate electrolyte. This procedure was chosen to minimize disturbances caused by washing. Washing could perturb particle to particle contact or could remove second phases. Any ionic conduction in the electrolyte would act in parallel to the electronic conduction in the cathode and increase the measured conductivity. Necessarily, the melt point of the electrolyte was not exceeded in these measurements. A conduction mechanism sustaining dc current would be difficult to rationalize for the solid electrolyte since the conducting ion, lithium, would not be discharged at the low potentials used in these measurements.

⁸L. J. Van Der Pauw, "A Method of Measuring the Resistivity and Hall Coefficient on Lamellae of Arbitrary Shape," Phillips Tech. Rev., Vol 20 p220 (1958/1959)

A summary of the measurements of this work is reported in Table 9 and Figures 21-24. The pre-test values measured at IFC are in good agreement with those reported previously at other institutions. Post-test values were obtained by extrapolation of the data in the figures and explained in the footnotes to the table. A value for nickel oxide is presented for reference.

Post-test conductivities for niobium doped ceria show orders of magnitude decrease from pre-test values. A higher activation energy for conduction is evidenced by an increase in slope of the post-test curve as shown in Figure 21. If the loss in conductivity were simply due to fewer carriers (electrons), consistent with niobium loss indicated by XRD, then the pre-test and post-test data should yield parallel lines. The increase in activation energy post-test may be due to carrier concentration increases with temperature in the ceria or in the second phase found post-test. This explanation would be consistent with the curve bending over at the highest temperatures of measurement post-test and is the justification for the dashed line extrapolation in the figure. DeGuire, et al⁹ has observed similar type behavior for niobium doped ceria. Measurements could not be conducted to high enough temperatures to allow a rational extrapolation of the data. Therefore, the extrapolation was made with a line parallel to the pre-test conductivity line at a level consistent with the observed increase in cell internal resistance, see the Section "iR Compensation." The smooth intersection of extrapolated and measured curves indicates internal consistency in this argument. IFC recognizes that this approach was less than ideal.

The conductivity of lithium manganite was the only sample to decrease in activation energy. This may be due to the gradual shift in phases of this cathode as described in the section under crystallography.

Lithium ferrite increases activation energy and conductivity as a result of soaking in the cathode environment. The increase in conductivity may be due to better distribution of dopant (lithium cobaltite phase disappears in XRD) and better particle to particle contact due to ripening (SEM micrographs).

YIG conductivities in Figure 24 are the most well behaved of the cathode materials studied. The pre-test and post-test fits to the data are nearly parallel while the post-test conductivities are lower. Dopant loss by leaching is consistent with this change and supported by electron microprobe analyses.

Table 9. Conductivities (S/cm) of Alternate Cathode Materials at 650°C

Material	Reported Conductivity	Pre-Test ^d	Post-Test ^{d,e}
Nb:CeO ₂	0.13 ^a	2.2 x 10 ⁻² (7.4 x 10 ⁻²)	2.3 x 10 ⁻³ (7.9 x 10 ⁻³)
Mg:Li ₂ MnO ₃	0.05 ^b	9.6 x 10 ⁻³ (4.6 x 10 ⁻²)	1.0 x 10 ⁻³ (4.8 x 10 ⁻³)
Co:LiFeO ₂	0.04-0.1 ^b	4.8 x 10 ⁻³ (5.8 x 10 ⁻²)	1.9 (23)
Ca,X:YIG	0.5 ^c	8.0 x 10 ⁻¹ (2.9)	4.2 x 10 ⁻² (1.5 x 10 ⁻¹)
^{a)} Footnote No. 4 ^{b)} Reference in Figure 1 ^{c)} Verbal Quote from S. Elangovan of CERAMATEC (8/91) on Porous Disc ^{d)} Measured Values, Parentheses – Corrected for Porosity – Bruggeman Factor 2 ^{e)} Extrapolated from Figures			

⁹Dequire, Shingler & Dincer, op.cit. pg 3-8

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Figure 21. Electronic Conductivity of Nb Doped Ceria in Dry ROX-3

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Figure 22. Electronic Conductivity of Mg Doped Li_2MnO_3 in Dry ROX-3

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Figure 23. Electronic Conductivity of Co Doped Lithium Ferrite in Dry ROX-3

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Figure 24. Electronic Conductivity of Doubly Doped YIG in Dry ROX-3

DISCUSSION

The purpose of this study was to test the stability of alternate materials in the complete cathode environment. IFC has shown that a viable commercial molten carbonate fuel cell must operate at 60 psia or higher. Any alternate material must be stable in this environment. Operation at this higher pressure was simulated in this corrosion test at one atmosphere with the Sim-Mix gas in which the oxygen and carbon dioxide partial pressures are four times those in ROX-3.

Li:NiO

Problems with nickel oxide solubility and shorting in full cells is well documented.

Performance of nickel oxide in the corrosion rig was limited by gas phase polarization in ROX-3 due to cell hardware. Good agreement with the IFC cathode performance model was obtained with MCO-D.

Measured values for surface area and performance were in agreement with typical IFC cathodes.

Nb:CeO₂

Ceria is phase, grain size, and surface area stable. Neither ceria nor niobium oxide migrate during the corrosion experiment. Niobium oxide dopant loss is indicated by XRD and corroborated by conductivity decrease and high cell resistance increase. This loss correlates with the introduction of the higher oxidizing atmosphere of the Sim-Mix gas rather than time at temperature. Niobium oxide exsolution is then thermodynamically controlled by the solubility dependence on oxygen pressure, rather than kinetically controlled by diffusion. Niobium oxide loss as the oxygen pressure increases is consistent with the defect chemistry of ceria.

Electrochemically, ceria is a much poorer catalyst than nickel oxide. The catalytic properties are further reduced by niobium oxide exsolution. The enrichment of niobium oxide on the surface during cooling from the sintering temperature could be the cause of the poor catalytic properties of the ceria cathode and is speculation at this point. The conductivity of ceria with other dopants has been investigated and the catalytic behavior could also be investigated.

Mg:Li₂MnO₃

The lithium manganite cathode was composed of several phases. Operation in the cathodic environment caused a partial shift from the monoclinic to the spinel phase, a decrease in grain size, and an increase in surface area. Manganese was found in the matrix post-test indicating a solubility in the electrolyte, this seems at odds with the observed increase in surface area. Reconciliation of these facts is possible if a slight solubility of the monoclinic phase in the electrolyte is assumed.

The performance of the cathode slightly increases with time. This increase may be attributable to the increase in surface area.

The decrease in the electronic conductivity with time is consistent with Mg loss. MgO is soluble in molten carbonate. The observed phase change which involves a change in stoichiometry may play a role in the conductivity decrease.

The stability of the performance of this cathode suggests further experimentation to optimize the microstructure with respect to the other cell components.

Co:LiFeO₂

Lithium ferrite is phase stable. The cathode contained excess dopant as a second phase, lithium cobaltite. This second phase leached out during the course of the experiment leaving pure doped cubic ferrite. Cobaltite and ferrite seem to be quite soluble in the carbonate as suggested by their migration.

Electronic conductivity increased substantially over the course of the test. A combination of two effects are probably responsible. It is possible additional cobalt was incorporated into the ferrite structure with time at operating temperature. Also, a large amount of grain growth probably increased the particle to particle contact area increasing the measured conductivity.

Particle ripening decreases the surface area, yet the performance of this cathode increases with time. Cell resistance is similar to that of nickel oxide possibly because lithium ferrite undergoes some amount of sintering at operating temperatures assuring good contact with the current collector. Optimizing performance based on increases in surface area will be effective only initially since the surface area cannot be retained.

Both cobalt and nickel can be reduced at anodic potentials in full fuel cells. The long term effects of cells containing cobalt should be assessed for shorting.

Ca,X:YIG

XRD identifies this compound as cubic YFeO₃ rather than garnet Y₃Fe₅O₁₂. The IFC assignment is consistent with the existence of second phases containing iron. However identified, the primary phase is stable in carbonate. The second phases containing spinels of iron and the proprietary dopant, X, leach during testing. The high migration of iron and X may be due to these second phases rather than solubility of the YIG phase. Absence of yttrium in the matrix, surface area stability, and only minor grain growth support the insolubility of YIG.

Electronic conductivity decreases with time. Possibly, dopants are leached from the material since both are soluble in carbonate. Cell resistances initially decrease but then increase again and are possibly the cause of the performance decrease from 500 to 1508 hours.

Previously, IFC found YIG to be unstable when in contact with molten carbonate and alumina when substantial conversion of YIG to lithium ferrite occurred. Later experiments, prior to this report, with YIG in contact with lithium aluminate and carbonate showed stability.

YIG seems to be a promising material. The stability with respect to dopant loss should be examined with purer materials.

RECOMMENDATIONS

Further work:

Ceria

- Look at other dopants such as tungsten oxide

Lithium Manganite

- Optimize performance by increasing surface area
- Run in cells saturated with MgO

Lithium Ferrite

- Prepare starting material as single phase
- Determine whether dopant is leached from lithium ferrite, itself
- Optimize cathode structure based on large grains
- Check shorting and long term stability in full cells, manganese may be a better dopant if cobalt leads to shorting

Yttrium Iron Garnet

- Identify the crystal phase
- Prepare starting material as single phase
- Use alternate dopants that are not leached by the electrolyte
- Optimize performance with microstructure

APPENDIX

Listed in this appendix are relevant data not presented in the main body of this report, but obtained under this contract.

Figures A1 to A5 present mercury intrusion porosimetry of the pre-test cathodes. Figures A6 to A15 show polarization (a) and Table (b) curves for alternate materials.

A-3

Figure A3. Cumulative Pore Volume (CC/G) vs. Pore Diameter for Co:LiFeO₂ Pre-Test

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Figure A4. Cumulative Pore Volume (CC/G) vs. Pore Diameter for Ca_xYIG Pre-Test

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Figure A5. Cumulative Pore Volume (CC/G) vs. Pore Diameter for Li:NiO Rig 2

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920506*Figure A6a. Polarization Curves of Nb:CeO₂ under Sim-Mix* 12292-18
920506*Figure A6b. Tafel Plots for Curves in Figure A6a*

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Figure A7a. Polarization Curves for Mg:Li₂MnO₃ under ROX-3

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Figure A7b. Tafel Plots for Curves in Figure A7a

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Figure A8a. Polarization Curves for Mg:Li₂MnO₃ under MCO-D

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Figure A8b. Tafel Plots for Curves in Figure A8a

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Figure A9a. Polarization Curves for Mg:Li₂MnO₃ under Sim-Mix

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Figure A9b. Tafel Plots for Curves in Figure A9a

Figure A10a. Polarization Curves for Co:LiFeO₂ under ROX-3

Figure A10b. Tafel Plots for Curves in Figure A10a

12292-27
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Figure A11a. Polarization Curves for Co:LiFeO₂ under MCO-D

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Figure A11b. Tafel Plots for Curves in Figure A11a

12292-29
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Figure A12a. Polarization Curves for Co:LiFeO₂ under Sim-Mix

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Figure A12b. Tafel Plots for Curves in Figure A12a

Figure A13a. Polarization Curves for $\text{Ca}_x\text{Y}_{1-x}\text{IG}$ under ROX-3

Figure A13b. Tafel Plots for Curves in Figure A13a

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Figure A14a. Polarization Curves for $\text{Ca}_x\text{Y}_{1-x}\text{IG}$ under MCO-D

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Figure A14b. Tafel Plots for Curves in Figure A14a

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Figure A15a. Polarization Curves for $\text{Ca}_x\text{X:YIG}$ under Sim-Mix

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Figure A15b. Tafel Plots for Curves in Figure A15a

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