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ADVANCED FUEL CELL DEVELOPMENT

Progress Report for
April—June 1984

by

R. D. Pierce, T. D. Claar,* D. W. Dees, R. J. Fousek,* T. D. Kaun,
G. H. Kucera, N. Q. Minh, F. C. Mrazek, R. B. Poeppel,*
J. L. Smith, J. R. Stapay, B. A. Baumert,[†] R. J. Herceg,[‡]
J. S. Hicks,** and J. R. Moreschi^{††}

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*Materials Science and Technology Division, ANL.

[†]Student Research Participant, Indiana University of Pennsylvania.

[‡]Pre-college Program Participant.

**Summer Research Student, Clemson University.

^{††}High School Faculty Research Program Participant.

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J. S. Hicks,** and J. R. Moreschi††

ABSTRACT

This report describes fuel cell research and development activities at Argonne National Laboratory (ANL) during the period April through June 1984. These efforts have been directed toward seeking alternative cathode materials to NiO for molten carbonate fuel cells. Particular emphasis has been placed on studying the relationship between synthesis conditions and the resistivity of doped and undoped LiFeO_2 and Li_2MnO_3 and on achieving a better understanding of the crystalline defect structures of the thermodynamically stable phases. To this end, several experimental assemblies (including synthesis, solubility, and sintering vessels and a high-pressure thermogravimetric analyzer) have been constructed to permit 10-atm operation. In addition, data on solubility and cathode cation- LiAlO_2 interaction were taken for NiO, Li_2MnO_3 , Mg-doped Li_2MnO_3 , LiFeO_2 , and ZnO at 1- and 10-atm pressure, and ion migration from LiFeO_2 and Li_2MnO_3 in the cell environment for 200 and 1000 h was examined.

Techniques are being studied for the preparation of thin electrode and electrolyte materials by tape casting. A study to provide improved understanding of anode creep and densification occurring under fuel cell conditions is under way.

SUMMARY

Cathode Development

Because of the problem of NiO cathode dissolution in molten carbonate fuel cells, the experimental work at ANL has concentrated principally on the investigation of alternative cathode materials. Currently, attention is focused on LiFeO_2 and Li_2MnO_3 and the effect of synthesis conditions on the resistivity of these materials in their doped and undoped states.

*Materials Science and Technology, ANL.

†Student Research Participant, Indiana University of Pennsylvania.

‡Pre-college Program Participant.

**Summer Research Student, Clemson University.

††High School Faculty Research Program Participant.

Resistivity Studies of Alternative Cathode Materials

Studies to determine the relationship between synthesis conditions and resistivity have continued. The effects of carbonate salt composition, gas composition, and copper doping on the measured resistivity of LiFeO_2 were examined. The salt composition and copper doping had no apparent effect. However, samples prepared in air showed lower resistivity ($\sim 3 \Omega \cdot \text{cm}$) than those prepared in mixtures of 30% CO_2 with various oxygen contents ($\sim 200 \Omega \cdot \text{cm}$). The resistivity of undoped LiFeO_2 was not affected by oxygen partial pressure or by carbon dioxide partial pressures as low as 2.5%. The effect of even lower carbon dioxide partial pressures will be examined.

Studies are under way to show the effect of sintering atmosphere on the resistivity of undoped LiFeO_2 . The resistivity of LiFeO_2 , prepared in air, was unchanged by sintering in a 30% CO_2 -air mixture. The study will also examine the effect of air sintering on a sample of LiFeO_2 prepared in 30% CO_2 -air.

The effect of gas composition on the resistivity of magnesium-doped and undoped Li_2MnO_3 was studied. For undoped Li_2MnO_3 , changes in resistivity were seen; however, there was no definite pattern with respect to either oxygen or carbon dioxide partial pressures. This behavior cannot be explained, at present. All samples of magnesium-doped Li_2MnO_3 prepared in high carbon dioxide ($> 30\%$) mixtures at atmospheric pressure had LiMnO_2 as a major phase and the expected Li_2MnO_3 as a medium to minor phase.

Related activities included a literature survey to identify methods that would aid in defining the crystalline defect structure of the cathode materials.

New Test Apparatus

Because pressurized operation of large fuel cell plants is desirable, several experimental assemblies capable of 10-atm operation are being built. The apparatus includes synthesis, solubility, and sintering vessels and a high-pressure thermogravimetric analyzer. To provide base-line data for the 10-atm studies, two 40-g batches of undoped LiFeO_2 have been prepared in air at 1 atm with excess carbonates.

Solubility of Alternative Cathode Materials

The solubilities of tape-cast cathode materials (NiO , LiFeO_2 , Li_2MnO_3 , and ZnO) laminated to electrolyte structures were determined at 925 K and 1 and 10 atm pressure of 24% CO_2 -12% O_2 -44% N_2 -20% H_2O . The solubility did not increase markedly with pressure, but the 1-atm test employed 62 mol % Li_2CO_3 - K_2CO_3 and the 10-atm test, 70 mol % Li_2CO_3 - K_2CO_3 .

The interaction of dissolved cations with LiAlO_2 was also examined. The data are not definitive; further studies are needed to assess the degree of interaction.

Cathode Material Migration Studies

Migration tests have been run for cells with Li_2MnO_3 and LiFeO_2 cathodes, using moist electrode gases. The 200-h tests indicate that these materials have significantly better stability than NiO . After a 1000-h test with a Li_2MnO_3 cathode, the electrolyte structure contained 180 ppm Fe, 95 ppm Mn, 550 ppm Cr, and 160 ppm Ni; however, corrosion products from the 304 SS hardware may account for a significant fraction of these values. Subsequent long-term tests will employ cell hardware that has been gold-plated on the appropriate surfaces.

Cathode Bed Resistivity Measurements

In an operating cell, the resistivity of a non-sintered, tape-cast cathode is a function of particle contact resistance, electrolyte volume, porosity, and cathode material resistance. A non-lithiated NiO particle bed, containing no electrolytes, was studied using complex impedance measurements. A resistance of 0.85Ω was determined from a complex impedance plot; a value of 0.62Ω was calculated for this material. The results suggest 30% particle-to-particle contact resistance.

Component-Structure Development and Evaluation

Cathode Structure Development

Work on cathode structure development this quarter was directed toward mercury porosimetry measurements on sintered bodies produced from tapes containing pore formers. The data indicate that the addition of pore formers increased the total porosity from 30 to 45% and the pore size range from $<2.5 \mu\text{m}$ dia to $2.5\text{--}6 \mu\text{m}$ dia.

Evaluation of Anode Creep Resistance

A study to improve the understanding of anode creep and densification occurring under fuel cell conditions is under way. The microstructures of several pre-test and post-test anode samples were examined by scanning electron microscopy. The examination showed little or no microstructural change.

I. INTRODUCTION

The advanced fuel cell studies at ANL are part of the DOE Advanced Fuel Cell Program. The objective of this DOE program is to reduce the technical uncertainties with fuel cells so that manufacturers and users can introduce high-efficiency generating systems, which have the capability of operating on coal or other fuels. At the present stage of development, the primary thrust of the ANL program is to provide supporting research and development that pursues fundamental understanding of fuel cell behavior and investigates alternative stack concepts.

The present molten carbonate fuel cells consist of a porous nickel anode, a porous lithiated nickel oxide cathode, an electrolyte structure that separates the anode and cathode and conducts only ionic current between them, and appropriate metal housings or, in the case of stacks of cells, intercell separator sheets. The cell housings (or separator sheets) bear upon the electrolyte structure to form a seal between the environment and the anode and cathode gas compartments. The usual electrolyte structure is a composite of discrete LiAlO_2 particles and a mixture of alkali metal carbonates. The carbonates are liquid at the cell operating temperature of about 650°C (925 K). At the anode, hydrogen and carbon monoxide in the fuel gas react with carbonate ion from the electrolyte to form water and carbon dioxide while giving up electrons to the external circuit. At the cathode, carbon dioxide and oxygen react and accept electrons from the external circuit to form carbonate ion, which is conducted through the electrolyte to the anode. In a practical cell stack, CO_2 for the cathode probably would be obtained from the anode exhaust.

It has become apparent that for pressurized operation, which is desirable for large power plants, nickel dissolution from the NiO cathode and deposition of metallic nickel in the electrolyte will prevent the attainment of the 4×10^4 h lifetime desired for commercial cells. The evaluation of possible alternative cathode materials is our principal current activity. We are also investigating anode densification mechanisms.

II. CATHODE DEVELOPMENT

A. Resistivity Studies of Alternative Cathode Materials

Because of the problem of NiO cathode dissolution in molten carbonate fuel cells, the experimental work at ANL is concentrated principally on the investigation of alternative cathode materials. Currently, attention is focused on testing of LiFeO_2 and Li_2MnO_3 and the effect of synthesis conditions on the resistivity of these materials in their doped and undoped states.

1. LiFeO_2 (N. Q. Minh)

The effects of dopant and material preparation conditions are under investigation for LiFeO_2 . During the past quarter, copper doping of LiFeO_2 was attempted. The effect of the variation in the partial pressures of oxygen and carbon dioxide atmosphere during the synthesis of undoped LiFeO_2 was also investigated.

The experimental procedure used to prepare Cu-doped LiFeO_2 with a Fe/Cu ratio of 10/1 was similar to that described in the previous quarterly for Ni-doped material. Preparation conditions and X-ray diffraction results are summarized in Table 1.

Table 1. X-ray Diffraction (XRD) Results^a for Cu-doped LiFeO_2

Sample	Carbonate Treatment			XRD Before Sintering
	Carbonate Salt	Temp., °C	Gas	
FC-1P1	Stoichiometric Li_2CO_3	700	Air	LiFeO_2 , $a = 4.150 \text{ \AA}$ + very minor CuO
FC-1P2	$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic	700	Air	LiFeO_2 , $a = 4.156 \text{ \AA}$
FC-1P3	Stoichiometric Li_2CO_3	700	30% CO_2 /Air	LiFeO_2 , $a = 4.162 \text{ \AA}$
FC-1P4	$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic	700	30% CO_2 /Air	LiFeO_2 , $a = 4.160 \text{ \AA}$

^aAll X-ray diffraction data given in this report were obtained by B. S. Tani, Analytical Chemistry Laboratory, ACL.

The X-ray diffraction results show a larger lattice constant for the samples prepared under CO_2 -air. On the other hand, the Cu-doped LiFeO_2 samples prepared under air have a lattice constant similar to that of undoped LiFeO_2 ($a = 4.152$ to $4.156 \text{ \AA}$) prepared under similar conditions (ANL-84-64). Not enough information is available to give an explanation for this observation.

Figure 1 shows resistivities at different temperatures for Cu-doped LiFeO_2 . From Fig. 1, it can be seen that doped materials synthesized under air have low resistivities. Comparison of the resistivity data for Cu-doped LiFeO_2 with those for undoped LiFeO_2 prepared under similar conditions (see curves in Fig. 1) shows that the copper doping carried out in this study does not lead to significant change in the resistivity of LiFeO_2 . (The small differences observed in the resistivity are due mainly to differences in degree of shrinkage.)

Fig. 1.

Resistivity of Cu-doped LiFeO_2

The effect of the partial pressure of oxygen in the preparation atmosphere on the resistivity of undoped LiFeO_2 was investigated. Undoped LiFeO_2 samples were prepared with different carbonate salt compositions under atmospheres containing 30% CO_2 and different percentages of oxygen. X-ray diffraction results are shown in Table 2.

The resistivity of the undoped samples was measured in air. It has been found that the carbonate salt composition used in the preparation does not affect the resistivity of LiFeO_2 . Figure 2 shows the resistivity of LiFeO_2 prepared in Li_2CO_3 - K_2CO_3 eutectic under different atmospheres. From Fig. 2, it can be seen that the variation of the partial pressure of oxygen (in the range shown in Table 2) in the synthesis atmosphere containing 30% CO_2 does not affect the resistivity of LiFeO_2 .

Table 2. X-ray Diffraction Results for Undoped LiFeO_2 Prepared at 700°C under Different Atmospheres

Salt	X-ray Diffraction Results ^a			
	30% CO_2 -5% O_2 -65% He	30% CO_2 -15% O_2 -55% N_2	30% CO_2 -40% O_2 -30% He	30% CO_2 -70% O_2
Stoich. Li_2CO_3	LiFeO_2 , $a = 4.158 \text{ \AA}$ + very minor LiFe_5O_8	LiFeO_2 , $a = 4.158 \text{ \AA}$	LiFeO_2 , $4.158 \text{ \AA}$ + very minor LiFe_5O_8 or Fe_3O_4	LiFeO_2 , $4.158 \text{ \AA}$
Excess Li_2CO_3	LiFeO_2 , $a = 4.158 \text{ \AA}$	LiFeO_2 , $a = 4.158 \text{ \AA}$	LiFeO_2 , $a = 4.158 \text{ \AA}$	LiFeO_2 , $4.158 \text{ \AA}$
Li_2CO_3 - K_2CO_3 Eutectic	LiFeO_2 , $a = 4.158 \text{ \AA}$	LiFeO_2 , $a = 4.158 \text{ \AA}$	LiFeO_2 , $a = 4.158 \text{ \AA}$	LiFeO_2 , $4.158 \text{ \AA}$

^aCover-gas pressure, 1 atm.

Fig. 2.

Resistivity of LiFeO_2 Prepared under Atmospheres Containing Different Oxygen Concentrations

Results have been obtained for undoped LiFeO_2 samples prepared under 10% CO_2 -15% O_2 -75% He, 5% CO_2 -15% O_2 -80% He, and 2.5 % CO_2 -15% O_2 -82.5% He. Preparation conditions and X-ray diffraction results are presented in Table 3, and resistivity data are shown in Fig. 3 (for samples prepared with stoichiometric Li_2CO_3). Data for a sample prepared under 30% CO_2 -air are also included for comparison. The similar resistivity results for samples prepared

Table 3. X-ray Diffraction Results for LiFeO_2 Prepared at 700°C under Different Atmospheres^a

Salt	X-ray Diffraction Results		
	2.5% CO_2 -15% O_2 -82.5% He	5% CO_2 -15% O_2 -80% He	10% CO_2 -15% O_2 -75% He
Stoich. Li_2CO_3	LiFeO_2 , $a = 4.158 \text{ \AA}$ + very minor LiFe_5O_8	LiFeO_2 , $a = 4.158 \text{ \AA}$	LiFeO_2 , $a = 4.158 \text{ \AA}$
Excess Li_2CO_3	LiFeO_2 , $a = 4.158 \text{ \AA}$	LiFeO_2 , $a = 4.158 \text{ \AA}$	LiFeO_2 , $a = 4.158 \text{ \AA}$
Li_2CO_3 - K_2CO_3 Eutectic	LiFeO_2 , $a = 4.158 \text{ \AA}$	LiFeO_2 , $a = 4.158 \text{ \AA}$ + minor $\gamma\text{-LiFeO}_2$	LiFeO_2 , $a = 4.158 \text{ \AA}$

^aCover-gas pressure, 1 atm.

Fig. 3.

Resistivity of Undoped LiFeO_2
Prepared under Atmospheres
Containing Different CO_2
Partial Pressures

in atmospheres containing 2.5-30% CO_2 suggest that the effect of CO_2 partial pressure in the preparation on the resistivity of LiFeO_2 occurs at less than 2.5% CO_2 . Preparation of LiFeO_2 samples in atmospheres containing less than 2.5% CO_2 is under way.

Another concern in the preparation of LiFeO_2 is the effect of sintering atmosphere on the properties of the material. To examine this effect, a small batch of LiFeO_2 was prepared under 30% CO_2 -balance air, and the prepared material was made into two pellets: one sintered under 30% CO_2 -balance air and the other under air. Conductivity measurements were done on the two pellets. Resistivity results are presented in Fig. 4, and X-ray diffraction results of the material before and after sintering are shown below.

<u>LiFeO_2 Prepared under 30% CO_2-Air</u>	<u>X-ray Diffraction</u>
Before sintering	LiFeO_2 , $a = 4.158 \text{ \AA}$
After sintering under air	LiFeO_2 , $a = 4.158 \text{ \AA}$
After sintering under CO_2 -Air	LiFeO_2 , $a = 4.158 \text{ \AA}$

The results from Fig. 4 and the X-ray diffraction indicate that the sintering atmosphere in this study had no effect on the resistivity of the LiFeO_2 . A batch of LiFeO_2 has been prepared under air. Resistivity of pellets of this material, sintered under air and CO_2 -air, will be measured.

Fig. 4.

Resistivity of LiFeO_2 Sintered under Different Atmospheres

2. Li_2MnO_3 (N. Q. Minh)

During this reporting period, the effect of the partial pressures and oxygen and carbon dioxide in the synthesis atmosphere on the resistivity of undoped Li_2MnO_3 was investigated. An attempt was also made to dope Li_2MnO_3 with magnesium and iron.

Magnesium-doped Li_2MnO_3 samples were prepared by the coprecipitation procedure previously described (ANL-83-89, p. 9). Undoped Li_2MnO_3 was prepared from hydroxide precipitate from manganese nitrate solution. The carbonate reaction for each sample was carried out at 700°C for 96 h under different atmospheres. Preparation details and X-ray diffraction results are summarized in Table 4.

Table 4. X-ray Diffraction Results for Mg-doped and Undoped Li_2MnO_3 Prepared under Different Atmospheres^a

X-ray Diffraction Results ^b			
	30% CO_2 -5% O_2 -65% He	30% CO_2 -15% O_2 -55% N_2	30% CO_2 -40% O_2 -30% He
Undoped	Li_2MnO_3 (283-1-9)	Li_2MnO_3 (283-1-6)	Li_2MnO_3 (283-1-7)
Mg-doped	---	LiMnO_2 major Li_2MnO_3 minor MgMnO_2 very, very minor (283-M1-6)	LiMnO_2 major Li_2MnO_3 minor (283-M1-7)
	30% CO_2 -70% O_2	67% CO_2 -33% O_2	
Undoped	Li_2MnO_3 (283-1-5)	Li_2MnO_3 (283-1-4)	
Mg-doped	LiMnO_2 major Li_2MnO_3 medium (283-M1-5)	LiMnO_2 major Li_2MnO_3 medium (283-M1-2)	

^aCover gas pressure, 1 atm.

^bNumbers in parentheses are sample numbers.

Undoped Li_2MnO_3 prepared under different atmospheres was shown by X-ray diffraction to be well crystalline. Magnesium-doped samples appear to be predominantly LiMnO_2 . One possible explanation for the presence of LiMnO_2 is its incomplete conversion to Li_2MnO_3 .

The resistivity of sintered pellets of undoped Li_2MnO_3 was measured in air for the temperature range of 300 – 700°C . (Sintered pellets of undoped material were about 81% dense.) The resistivity data obtained are shown in Fig. 5. For undoped Li_2MnO_3 , the resistivity of Li_2MnO_3 does not show a definite trend with varying oxygen partial pressure in the preparation. For example, the resistivities of the samples prepared under 30% CO_2 -70% air and 30% CO_2 -70% O_2 are about the same, whereas those under 30% CO_2 -40% O_2 -30% He and 30% CO_2 -5% O_2 -65% He are somewhat lower. More experiments with different oxygen pressures are required to clarify the effect of O_2 partial pressure.

Experiments to investigate the effect of partial pressure of carbon dioxide in the preparation atmosphere on the conductivity of Li_2MnO_3 were also conducted. In this study, undoped Li_2MnO_3 was prepared under three

Fig. 5.

Resistivity of Undoped Li_2MnO_3
Prepared under Different
Atmospheres

different cover gases: 2.5% CO_2 -15% O_2 -82.5% He, 5% CO_2 -15% O_2 -80% He, and 10% CO_2 -15% O_2 -75% He, at 1-atm pressure. X-ray diffraction results show Li_2MnO_3 as the only phase.

Resistivity results for two samples (5 and 10% CO_2) together with those for undoped Li_2MnO_3 prepared under 30% CO_2 -balance air are shown in Fig. 6. Again, the resistivity curves do not show a trend with varying carbon dioxide pressure. As stated earlier, it appears that more experiments are required to obtain information to explain this behavior.

During this reporting period, an attempt was also made to dope Li_2MnO_3 with iron. Two small batches of Fe-doped Li_2MnO_3 (one with $\text{Fe}/\text{Mn} = 1/20$ and one with $\text{Fe}/\text{Mn} = 1/10$) were prepared by coprecipitation from nitrate solution. The carbonate reaction was carried out under 30% CO_2 -70% air. For each iron dopant concentration, two samples (with and without an interdiffusion step) were prepared. Those samples are at various processing stages at this time. The resistivity of a pellet of Fe-doped Li_2MnO_3 ($\text{Fe}/\text{Mn} = 1/20$), prepared without an interdiffusion step and sintered at 1100°C for 4 h, was measured and is given in Fig. 7. This figure shows no significant difference in the resistivity of undoped and iron-doped ($\text{Fe}/\text{Mn} = 1/20$) samples prepared under similar conditions. X-ray diffraction shows a slight increase in the positions of diffraction lines in the iron-doped sample. The X-ray diffraction analysis of a sample with an interdiffusion step (about 1150°C for 100 h under air) shows the material as Li_2MnO_3 , with LiMnO_2 as a minor phase. Similar results were also obtained for Fe-doped Li_2MnO_3 with higher iron concentration ($\text{Fe}/\text{Mn} = 1/10$). Doped materials that contained a LiMnO_2 phase have been carbonate-treated again to convert LiMnO_2 to Li_2MnO_3 . Results will be reported in the next quarterly.

Fig. 6.

Resistivity of Li_2MnO_3 Prepared under Different CO_2 Partial Pressures

Fig. 7.

Resistivity of Fe-Doped and Undoped Li_2MnO_3

3. Related Activities

a. Cation-Valence Identification (G. H. Kucera, N. Q. Minh)

A better understanding of the relationship between the crystalline properties of the synthesized cathode materials and the measured electronic resistivities is needed to elucidate the crystalline defect structure

of these materials. A survey of the literature was conducted and a number of readily available methods with which the defect structure might be studied were identified; these include visible absorption spectrophotometry, wet chemical analysis, and X-ray diffraction analysis. While the first two methods do not yield information on atomic arrangements, they may provide quantitative assessments of the valence states of transition metal and/or dopant cations, thereby giving indications of defects in the doped and undoped materials. It is possible that the data from these three methods may be used to deduce the position of the dopant in the crystal structure. Tests to assess the effectiveness of these methods are under way.

As a first approach, samples of conductive but undoped LiFeO_2 have been submitted for wet chemical analyses. These data are not yet available.

These methods represent the initial approach to be used in understanding the synthesized cathode materials. Later, other tests, not amenable to doing large numbers of samples, such as neutron diffraction analysis, may be done on selected samples.

B. New Test Apparatus

(J. L. Smith, G. H. Kucera, J. S. Hicks,* J. R. Moreschi,[†]
R. J. Herceg,[‡] and J. R. Stapay)

At present, cathode materials are prepared (air or cathode gas), sintered, and tested (air only) at 1-atm pressure. Because pressurized operation (10 atm) of large fuel cell plants is expected, it seems unlikely that the 1-atm tests provide a realistic characterization of the cathode material properties. Therefore, several experimental assemblies, capable of 10-atm operation with typical cathode gas(es), are being constructed. These include synthesis, solubility, and sintering vessels and a high-pressure thermogravimetric analyzer.

The work on modification of the Ainsworth balance is continuing. The major items to be completed are the down tubes, the furnace and controllers, and the connection to the computer. The wiring of the balance and the interface electronics are complete. Work is now under way to write the software to operate the balance. One down tube is completely assembled and the second partially assembled. These are fabricated of Inconel 625 (1-in. OD x 0.35-in. wall) tubing with water jackets near the balance. When installed on the balance, these tubes will have a center-to-center spacing of five inches. This will require a special tube furnace with two tubes spaced five inches apart. The heater tubes to fabricate this furnace are on order, but have not yet been received. The furnace tubes will have individual temperature controllers, each with an over-temperature shut-off capability for reasons of safety. The parts for these controllers have been ordered. The wiring to the computer has been partially installed.

*Summer Student Research Program participant from Clemson University.

[†]High-School Faculty Research Program participant

[‡]Pre-college Program participant.

The work on the design of the pressurized conductivity apparatus has been delayed due to demands for other pieces of equipment. As this is a necessary test, work will resume as soon as possible.

The parts for a pressurized sintering apparatus are complete. The vessel must be hydrostatically tested and the furnace, thermocouples, etc., installed. The furnace runs on low-voltage DC current. A power supply has been repaired for use with the apparatus, but a temperature control system must be built.

Earlier investigations were done to determine the effect of gaseous environment at 1 atm on the measured electronic resistivity of both doped and undoped LiFeO_2 and Li_2MnO_3 . Current plans include the synthesis and study of doped and undoped materials produced under fuel cell conditions, i.e., 650°C in representative cathode gas(es) at 10-atm pressure.

Two 10-atm pressure vessels of Inconel were fabricated and the associated equipment, required for these experiments, ordered. Heating elements were replaced in two three-zone furnaces; the furnaces now operate as per their specifications. A safety review of these two experimental units is under way.

To provide base-line data for the 10-atm studies discussed above, two 40-g batches of undoped LiFeO_2 were prepared in air at 1 atm with excess (20 g) 70 mol % Li_2CO_3 -30 mol % K_2CO_3 . Portions of these batches will be used to test the feasibility of employing visible absorption spectrophotometry as a tool to identify cationic valence states. They will also be used for thermogravimetry studies, wet chemical analyses assessing cationic valence states, and conductivity measurements.

Synthesis of LiFeO_2 under representative cathode gas(es) will be initiated as soon as the gas mixtures are received from the vendor.

C. Solubility of Alternative Cathode Materials

(T. D. Kaun and B. A. Baumert*)

Solubility of alternative cathode materials (Li_2MnO_3 , LiFeO_2 , and ZnO) is being examined for temperature dependence and effects of humidity and electrolyte compositions. Low solubility is desirable for an electrode microstructure to resist sintering. Preparations are being made to examine solubility and electrode microstructure change ("ripening") at 10 atm of humidified cathode gas. Solubility of dopants for the alternative cathode materials is also being examined. Alternative cathode materials are expected to require doping to impart sufficient conductivity for use in a molten carbonate fuel cell. Leaching of dopant could lead to degradation of cell performance because of altered material conductivity.

Because earlier tests indicated incorporation of zinc into the LiAlO_2 matrix material, we initiated a task to examine the interaction of LiAlO_2 with other cathode-material constituents. If such interactions occur, LiAlO_2 could act as a sink for solubility products transported into the electrolyte matrix.

*Student Research Participant from Indiana University of Pennsylvania.

1. Effect of Gas Pressure on Cathode Material Solubility

Our current emphasis in cathode material solubility is the change in solubility with increasing cathode gas pressure. Tape-cast samples of cathode material laminated with LiAlO_2 (see ANL-84-64 for preparation procedure) were maintained for 400 h at steady-state conditions of 650°C , in 30% CO_2 -air humidified to 20% H_2O at 1.0 or 10.0 atm. Metallographic examination confirmed that good lamination of tape-cast layers had been achieved. In this approach, equilibrium is dependent upon diffusion of soluble species into the carbonate-wetted LiAlO_2 matrix (30 wt % Li_2CO_3 - K_2CO_3 and 70 wt % LiAlO_2). The 1-atm test used 62 mol % Li_2CO_3 - K_2CO_3 , and the 10-atm test used 70 mol % Li_2CO_3 - K_2CO_3 . The latter composition showed reduced NiO solubility in earlier testing with cyclic voltammetry (ANL-84-64). After exposure to the test conditions, the samples were prepared for analysis by abrading away the cathode layer from the LiAlO_2 layers. These samples were first treated with weak acid (1N HCl or carbonic acid) to dissolve the carbonates and were separated from the LiAlO_2 by filtration. Filtration was not complete due to the presence of extremely fine LiAlO_2 particles.

The ANL Analytical Chemistry Laboratory examined alternative separation methods, none of which was better than the above one. The separated LiAlO_2 was then treated with concentrated acid to leach any metals that may have combined with the LiAlO_2 . The results of analyses by inductively coupled plasma/atomic emission spectroscopy are presented in Table 5 and discussed below.

Table 5. Solubility Levels from Tape-cast Samples at 1 and 10 atm of 30% CO_2 -Air Humidified to 20% H_2O

Cathode Material	Solubility Results, ppmW ^a			
	@ 1 atm in 62 mol % LiCO_3		@ 10 atm in 70 mol % LiCO_3	
	from Salt	from LiAlO_2	from Salt	from LiAlO_2
Ni from NiO	37	54	70.3	73.3
Mn from Li_2MnO_3	10	100	6.5	31.8
Mg ^b from Mg-doped Li_2MnO_3	1100	60	1900	58
Fe from LiFeO_2	21 ^c	210 ^c	200 ^c	52 ^c
Zn from ZnO	28	3700	86	5110

^aThe ppmW levels are based on total sample weight of 30% carbonate and 70% LiAlO_2 .

^bLikely to be MgO, which is unincorporated Mg dopant (ANL-84-64).

^cComparable iron levels were observed in non- LiFeO_2 tests. Carbonate of 70 mol % LiCO_3 - K_2CO_3 tests had been contaminated with 200 ppmW Fe.

a. NiO

The solubility of NiO is expected to increase linearly with carbon dioxide partial pressure. The solubility results of Table 5 suggest that the 70 mol % Li_2CO_3 electrolyte improved NiO stability, since the tenfold increase in cathode gas pressure resulted in only a twofold increase in solubility. It is suggested that a cathode material migration test with 70 mol % carbonate be conducted to verify this result.

b. Li_2MnO_3

As our earlier tests indicated, the solubility of Li_2MnO_3 in carbonate 's consistently low and apparently is not appreciably affected by cathode gas pressure to 10 atm.

c. MgO

Unincorporated Mg-dopant had been identified in earlier samples as MgO. Its solubility appears to nearly double from the tenfold increase of cathode gas pressure, going from 0.37 to 0.63 wt % Mg, based on the carbonates alone.

d. LiFeO_2

The values for iron levels found in the carbonates and LiAlO_2 were quite close to those of the background levels. The LiFeO_2 solubility could be quite low. The results give no reason for concern over increased solubility due to cathode gas pressure increase.

e. ZnO

The results further support the earlier findings of zinc incorporating with LiAlO_2 . The cathode gas pressure of 10 atm resulted in only 30 wt % higher zinc present in the LiAlO_2 . It may be that these levels, 0.7 wt % Zn in LiAlO_2 , are nearing saturation.

f. Conclusion

The data presented in Table 5 suggest that the cathode cations may interact with LiAlO_2 . However, it is possible that the values given are higher than warranted due to sample preparation (abrading of the cathode layer may have introduced cathode particles into the electrolyte layer). Further studies to examine this interaction must be done to better define the values.

A repeat of the cathode gas solubility tests at 10 atm is under way. Some difficulty in maintaining humidity levels occurred in the first test, and a repeat of this test will increase the reliability of the results.

Portions of the test samples were mounted in epoxy and polished for an examination of electrode microstructural change. The first set included samples exposed to 1-atm cathode gas for 400 h, and 10-atm cathode gas for 400 h. Scanning electron micrographs were taken at 2000X. No apparent

particle growth was observed, but it was concluded that the carbonates would have to be washed from the samples to enable a reliable examination. Therefore, we are planning to hold the samples in the repeat test for longer time, >1000 h, to allow greater differentiation to occur due to the 10-atm conditions.

2. Interaction of LiAlO₂ with Cathode Solubility

A test was undertaken to investigate possible interaction of LiAlO₂ with cations of the following metals: Cr, Fe, Mg, Mn, and Zn. This test was brought about by the observation that ZnO had been transported across the electrolyte; the issue under investigation is whether the zinc interacted with the LiAlO₂ structure, which acted as a "sink" in the electrolyte for cathode solubility products. One mechanism might be doping of the LiAlO₂ by substitution of the dissolved ions for aluminum. Accordingly, a quantity of the potential doping material equivalent to a 1 to 10 at. ratio of dopant to aluminum, was added to 1 g of Degussa γ -Al₂O₃, as calculated according to the equation:

where M refers to the doping ion. Because 1/11 of the Al atoms present will be replaced by metal ions, the atomic ratio of metal added to Al present is 0.1:1.

The corresponding amounts of the metal oxides and Al₂O₃ were placed in alumina crucibles, which were heat treated in an oven furnace at 1100°C for over 100 h to allow solid-state diffusion to occur. A 78.7 mol % Li₂CO₃-balance K₂CO₃ mixture, which has a liquidus temperature of approximately 620°C, was then added to the sample. After the lithium had reacted with the aluminum, the salt consisted of 62 mol % Li₂CO₃-balance K₂CO₃. The purpose of adding the carbonate salt is to simulate fuel cell conditions and to provide ionic migration.

The samples were exposed to cathode-side conditions in an upright tube furnace. Each alumina crucible containing a sample was placed on a different shelf of a rack with shelves spaced one-inch apart. The furnace was set for 650°C and 1 atm of pressure (a 30% CO₂-balance air mixture). The samples were removed after 100 h, the carbonates were washed out with water, and the samples were dried at 1000°C for 25 hours.

X-ray diffraction was used for identifying the reaction products, given in Table 6. The X-ray data do not give clear evidence of cathode cation interaction with LiAlO₂. Owing to the uncertainty in this data, further studies are warranted.

D. Cathode Material Migration Studies (F. C. Mrazek, J. R. Stapay, and J. L. Smith)

Earlier migration cell tests were completed at 650°C for 200 h, using moist electrode gases* and Li₂MnO₃ or LiFeO₂ cathodes. The test results

*Anode gas: 0.64 H₂, 0.16 CO₂, 0.20 H₂O; cathode gas: 0.53 CO₂, 0.27 O₂, 0.20 H₂O.

Table 6. Reaction Products of Doping Tests Observed by X-ray Diffraction Analysis

Sample	Potential Doping Ion Present	Phases Indicated				
		Major	Medium	Minor	Very Minor	Very, Very Minor
1	Mn	γ -LiAlO ₂	LiAl ₅ O ₈	Spinel type ^a		
2	Cr	γ -LiAlO ₂	LiAl ₅ O ₈			LiCrO ₂ possible
3	Fe	γ -LiAlO ₂	LiAl ₅ O ₈			LiFe ₅ O ₈
4	Mg	Spinel Type ^b & γ -LiAlO ₂				MgO
5	Zn	ZnAl ₂ O ₄ ^c & γ -LiAlO ₂				ZnAl ₂ O ₄

^a Similar to LiMn₂O₄ and LiMg_{0.5}Mn_{1.5}O₄; may be a solid solution of Li-Al-Mn-O system.

^b Similar to MgAl₂O₄ and LiAl₅O₈.

^c Actually similar to both ZnAl₂O₄ and LiAl₅O₈.

indicate that these cathode materials have significantly better stability than NiO. It naturally follows that longer tests should be run to enable better extrapolation of the stability test results.

Two cells (13A and 13B), employing the above-mentioned gases and cathode materials, were operated for 1000 h during this reporting period. Operation of Cell 13A, containing a LiFeO₂ cathode, was terminated due to a sudden drop in voltage after 359 h at >1.08 V. Gross quantities of corrosion products were found throughout the electrolyte structure, indicating a severe short circuit. No migration information was obtained from this cell test. Cell 13B contained a Li₂MnO₃ cathode and was operated between 1.06 and 1.11 V for 1000 h. A single, thin, red-colored band was observed in the electrolyte structure; scanning electron microscopy/energy-dispersive X-ray analysis showed a high chromium content. Chemical analysis of the electrolyte structure for non-electrolyte cations showed 180 ppm Fe, 95 ppm Mn, 550 ppm Cr, and 160 ppm Ni.

Corrosion products from the 304 stainless steel hardware may be a significant fraction of these values. The next long-term test will include cell hardware that has been gold plated on the appropriate surfaces to prevent corrosion by the liquid carbonates.

E. Cathode Bed Resistivity Measurements (T. D. Kaun and D. W. Dees)

Measurements of cathode-bed resistivity are of interest as a basis for setting goals in cathode material conductivity. The current trend toward use of tape-cast cathodes would likely lead to simple particle-bed cathodes. Here, the cathode material resistivity is one of a number of factors which determine the overall cathode resistivity. Our objective is to provide insight to resistivity contributions from particle-particle contact, electrolyte volume, and microstructure operating conditions, as well as resistivity of the cathode material itself. The initial experiment examined a NiO tape-cast sample. Future experiments will examine lithiated NiO, carbonate-wetted lithiated NiO, and variations of promising new cathode materials. Tests can examine effects of varying compression loading, temperature, and cathode gas composition.

The complex impedance plot (Fig. 8) of the tape-cast NiO sample (area, 0.785 cm^2 ; thickness, 0.0254 cm ; 65% dense) between gold electrodes was derived from data generated by a Solartron frequency response analyzer. The resistivity of crystalline NiO¹ is reported to be about $10 \text{ } \Omega \cdot \text{cm}$. Therefore, the calculated resistance (from the Bruggeman equation²) for our NiO sample is $0.617 \text{ } \Omega$. The high frequency intersection of Z' , the real axis, at about $0.85 \text{ } \Omega$ indicates electrode-bed resistance (without contact-resistance to the gold electrodes). The results suggest that about 30% of the cathode resistance is due to particle-particle contacts. A lithiated NiO sample is being examined because lithiation reduces the resistivity of NiO by three orders of magnitude. We will make some equipment adjustments to improve the reliability of these measurements.

Fig. 8. Complex Impedance Plot for NiO Sample (area, 0.785 cm^2 ; thickness, 0.0254 cm ; 65% dense) at 923 K under 210 kPa (30 psi)

III. COMPONENT STRUCTURE DEVELOPMENT AND EVALUATION (T. D. Claar, R. J. Fousek, and R. B. Poeppel)*

A. Cathode Structure Development

Magnesium-doped lithium manganite is one of the potential replacements for nickel oxide in the cathode. The development work on this material has focused on fabricating a lithium manganite structure with "dual porosity" and a total porosity of 55-65%. Approximately half of the porosity is to be comprised of small pores ($\leq 1 \mu\text{m}$) and half larger pores ($\sim 10 \mu\text{m}$).

In the previous quarterly, we reported results obtained from tape casting of eight magnesium-doped lithium manganite slips, with and without addition of pore former. The micrographs we presented of three of the structures indicated that the appropriate microstructure could be obtained with the addition of pore former. The tape-cast slips were prepared by vibratory milling a spray-dried powder (Batch LMM-2) in an acrylic-based binder system (Cladan Cerbind 73131[†]). After vibratory milling to disperse the powder, the slips were de-gassed by evacuating to 0.5 atm and then cast onto a Teflon substrate with a moving doctor blade. Of the three slips, one was cast without the addition of pore former (LIM-16-5); another was cast with Avicel PH-105 MCC pore former at a MCC/ceramic ratio of 0.17 (LIM-14-5); and the third was cast with corn starch pore former at a starch/ceramic ratio of 0.17 (LIM-17-2). Disk-shaped specimens were punched from each tape fired. The details of the firing schedule were also reported in the previous quarterly report. Since the micrographs indicated that we had obtained fairly good results with the addition of pore formers, we decided to obtain mercury intrusion porosity data on the three structures.

The three slips were submitted for mercury intrusion porosimetry[‡]. The porosimetry data are displayed graphically in Fig. 9. Although encouraging, the data fall short of our goals for dual porosity. The structure of the material prepared without pore former, LIM-16-5, contains less than 5% of its porosity in pores with diameter $< 1 \mu\text{m}$ and a total porosity of about 30%. Eighty percent of the porosity is due to pores $< 2.5 \mu\text{m}$ diameter. In the other two slips, LIM-17-2 and LIM-14-5, the addition of pore former increased the total porosity to 40-45%. The added porosity is in the 2.5-6 μm diameter range.

The conclusions drawn from the mercury porosimetry are: (1) the initial porosity, without pore former, lacks the submicron diameter pores we are seeking at the small end of the pore size distribution; and (2) although the addition of pore former added new large pores, these pores in the sintered structure are not quite as large as needed. These preliminary data were obtained from materials prepared without carbonate electrolyte and fired at 1250°C. Based on these results, we prepared tape-casting slips containing both the magnesium-doped lithium manganite material and carbonate electrolyte (Table 7). These were cast on Teflon. Disks (1-in. dia) were cut and heated

*Materials Science and Technology Division, ANL.

[†]Cladan Technology, Inc., San Marcos, CA.

[‡]Institute of Gas Technology, Chicago, IL.

Fig. 9. Pore Size Distribution Obtained by Mercury Intrusion Porosimetry for Three Tape Cast and Fired Cathode Structures (LIM 16-5, no pore former; LIM 14-5, MCC pore former; and LIM 17-2, corn starch used as a pore former).

Table 7. Summary of Mg-doped Li_2MnO_3 Cathode Tapes

	Composition, g						
	LIM-19	LIM-20	LIM-21	LIM-22	LIM-23	LIM-24	LIM-25
Cerbind 73131 binder ^a	50	50	50	50	50	50	50
Kellogg Z-3 fish oil ^b	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Li_2MnO_3 powder ^c	30	30	30	30	30	30	30
Pore former	-	5 ^d	5 ^e	-	-	-	-
$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3^f$	1.5	1.5	1.5	3.0	4.5	7.5	10

^aCladan Technology, Inc., San Marcos, CA.

^bSpencer-Kellogg Division of Textron, Inc., Buffalo, NY.

^cBatch No. LMM-5 (-230 mesh).

^dCorn starch.

^eAvicel PH-105 microcrystalline cellulose, FMC Corp., Philadelphia, PA.

^f62 mol % Li_2CO_3 -38 mol % K_2CO_3 , premelted and pulverized.

to 650-700°C in order to burn out the organics and fuse the carbonate. Microstructural analysis of these materials is in progress, and the results will be presented in the next reporting period.

B. Evaluation of Anode Creep Resistance

The objective of this activity is an improved understanding of the anode creep and densification that occur under fuel-cell operating conditions. An apparatus is being assembled in which anode creep may be measured under controlled conditions of mechanical load, temperature, and chemical environment.

During this quarter, several anode samples were identified for preliminary analysis. These samples include the porous nickel anodes taken from cells SQ-28 and SQ-33 tested at ANL during 1981 and 1982.

The anode of cell SQ-28 (ANL-82-67, pp. 17-19) was fabricated with a gas barrier of fine nickel on the anode at the anode-tile interface. The barrier was sprayed onto the anode surface as NiO and subsequently reduced to the metal by sintering in a He-6% H₂ atmosphere at 750°C for 3 h.

The microstructure of the material used in SQ-28, as it appeared before cell testing, is shown in Fig. 10a. A sample of anode material taken from the cell after testing was soaked in 10% acetic acid solution to remove carbonate. A 0.2889-g sample lost 0.0465 g when soaked in 40 mL of the dilute acid. The scanning electron micrograph (Fig. 10b) reveals little change in the microstructure. The bubble barrier is visible on the top surface. In Fig. 10c, the bubble barrier is shown at higher magnification.

The microstructure of the material used in SQ-33, as it appeared before cell testing, is shown in Fig. 11a. Cell SQ-33 was run for 1413 h to study cathode dissolution (ANL-83-34, pp. 27-28). A sample weighing 0.2910 g taken from the cell lost 0.0482 g when soaked for 24 h in 40 mL of 10% acetic acid to remove carbonate. The microstructure shown in Fig. 11b appears unaffected by the cell operation.

Cursory examination of chromium distribution in these samples did not reveal any startling effects of cell operation. The chromium distribution will be examined in greater detail, and creep testing will begin during the next quarter.

Fig. 10. Microstructure of the Porous Nickel Anode Material Used in Cell SQ-28 (a) before and (b) after Cell Test. The nickel bubble barrier is visible on the top surface (c). At larger magnification, the bubble barrier appears with a more coarse porosity as compared with the nickel anode.

Fig. 11. Microstructure of the Porous Nickel Anode Material Used in Cell SQ-33 (a) before and (b) after Cell Test

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