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ADVANCED FUEL CELL DEVELOPMENT

**Progress Report for
January—March 1977**

by

**J. P. Ackerman, K. Kinoshita, J. W. Sim,
R. Swaroop, and P. A. Nelson**

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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CHEMICAL ENGINEERING DIVISION
ADVANCED FUEL CELL DEVELOPMENT

January—March 1977

by

J. P. Ackerman, K. Kinoshita, J. W. Sim,
R. Swaroop, and P. A. Nelson

ABSTRACT

This report describes advanced fuel cell research and development activities at Argonne National Laboratory (ANL) during the period January - March 1977. These efforts have been directed toward understanding and improvement of molten carbonate electrolyte fuel cells operating at temperatures near 650°C.

A primary focus of the work has been on developing electrolyte structures which have high strength and conductivity, as well as good electrolyte retention, and on developing methods of synthesis for electrolyte structures that are amenable to mass production. Several synthesis methods have been investigated, and at least one appears to yield a highly desirable product and to greatly simplify production.

Cell testing is essential for understanding and evaluating individual component behavior and the interactions of the components under realistic operating conditions. Most of the testing to date has been conducted in a 2 3/4-in.-dia cylindrical cell with Type 316 stainless steel housings and current collectors, a nickel anode, and a nickel oxide cathode. Reproducible cell operation has been achieved in these cells, and operational parameters have been brought under control. Necessary improvements in cell components have been defined, and a systematic program of optimization has begun.

Components evaluation and development include post-test analysis and evaluation of all the cell components and materials as well as development of out-of-cell diagnostic tests for the individual components. Particular attention is being paid to evaluation of the physical properties of the electrolyte and to corrosion of metallic materials in the cell housings.

SUMMARY

Electrolyte Development

Preparation and Characterization of LiAlO_2 . The synthesis of LiAlO_2 by reaction of alumina with mixtures of alkali carbonates or with alkali hydroxides was studied. The effect of variables, such as reaction time, temperature, type of alumina, and methods of mixing reactants, on the product's allotropic

form and particle morphology was investigated using X-ray diffraction and scanning electron microscopy.

The reaction of $\gamma\text{-Al}_2\text{O}_3$ with mixtures of Li_2CO_3 and K_2CO_3 required temperatures of 600-700°C; $\alpha\text{-LiAlO}_2$ was the major product of this reaction. Reaction of LiOH (or mixtures of LiOH and KOH) with $\gamma\text{-Al}_2\text{O}_3$ below 450°C produced only $\beta\text{-LiAlO}_2$. At 450°C, reaction of $\alpha\text{-Al}_2\text{O}_3$ with hydroxides produces mostly $\gamma\text{-LiAlO}_2$ and some $\beta\text{-LiAlO}_2$. The major product of the reaction with hydroxides at 600°C is $\gamma\text{-LiAlO}_2$, regardless of the Al_2O_3 allotope used.

The LiAlO_2 particles can be classified by particle shape as square bipyramids, rods, platelets, and clumps. Rods of $\beta\text{-LiAlO}_2$ were always formed by low temperature reaction of $\gamma\text{-Al}_2\text{O}_3$ with LiOH/KOH mixtures. Platelets of $\beta\text{-LiAlO}_2$ always resulted from reaction of LiOH and $\gamma\text{-Al}_2\text{O}_3$. In high temperature (>600°C) preparations, $\gamma\text{-LiAlO}_2$ usually appears as square bipyramidal particles of very regular habit. In other cases, platelets of $\alpha\text{-LiAlO}_2$ and clumps of $\alpha\text{-}$ or $\beta\text{-LiAlO}_2$ were observed. Except in the case of bipyramidal $\gamma\text{-LiAlO}_2$, it is not possible to definitely assign an allotropic form to particles by observation of their habit.

Phase and Structural Stability of LiAlO_2 . Investigations of long-term changes in LiAlO_2 allotropy and particle shape and size were begun, using both in-cell and controlled-environment testing. Only a few results have been obtained, but it appears that allotropic transformations are more rapid in the cell wet-seal area than in the central area. $\beta\text{-LiAlO}_2$ was seen to transform completely to $\gamma\text{-LiAlO}_2$ in less than 100 hr in a dry CO_2 environment in the presence of lithium and potassium carbonates at 700°C. This effort has just begun; the amount of information to date is not sufficient for more than speculation.

Preparation of Electrolyte Tiles. Powdered mixtures of LiAlO_2 , Li_2CO_3 and K_2CO_3 were pressed into structures called tiles prior to use in fuel cells. The pressing was carried out at 6800 psi and 470-490°C in a high-temperature steel (H-21) die which was sprayed with a protective graphite coating. Variations on these conditions were not studied, but lower temperatures or pressures may be suitable.

Cell Testing

Cell testing at ANL is conducted primarily for evaluation of cell components. Ten cells have been operated to date. The performance and reliability of the cells and test procedures are continually being increased as understanding of the components and operating procedures is built up. Cell testing and component properties are reported in this section; post-test analysis and electrolyte development are in separate sections.

Component Analysis and Development

Post-test analyses and evaluations of separator and cell housing materials are being conducted and test methods are being developed. Corrosion, wet-seal leakage, and electrolyte creep are all considerably more severe at the anode than at the cathode; it is apparent that the metal of the anode wet seal must be protected with some kind of passive coating. Cell housings are being aluminized in the wet-seal area for this purpose. Experiments are also being

planned to evaluate the corrosion behavior of selected metals in the wet-seal area. Simple nondestructive physical tests for pre-test tile evaluation are described, as is a static creep test for tile strength at temperature.

I. INTRODUCTION

The advanced fuel cell studies at Argonne National Laboratory (ANL) are part of the ERDA Second Generation Fuel Cell Program. This ERDA program has as its goal the earliest possible introduction of coal-fueled, high-efficiency electric generators based on molten carbonate fuel cells, and is being carried out primarily by industrial contractors. At the present stage of development, the primary thrust of the program is directed toward development of the fuel cell itself.

Molten carbonate fuel cells consist of a porous nickel alloy anode, a porous nickel oxide cathode, an electrolyte structure separating the anode and cathode, and appropriate metal cell housings or, in the case of stacks of cells, cell separator plates. The cell housings (or separator plates) bear upon the electrolyte structure to form a seal between the environment and the anode and cathode gas compartments. The electrolyte structure, which is commonly called a "tile," is a composite structure of solid LiAlO_2 particles and a mixture of alkali metal carbonates which are liquid at the cell operating temperature of 650°C . At the anode, hydrogen and carbon monoxide in the fuel gas react with carbonate ion from the electrolyte to form carbon dioxide and water, giving up electrons to the external circuit. At the cathode, carbon dioxide and oxygen react and accept electrons from the external circuit to re-form carbonate ion, which is conducted through the electrolyte to the anode. In a practical cell stack, CO_2 for the cathode would be obtained from the anode exhaust.

The ANL contribution to the program is intended to provide understanding of cell behavior and improved components and processes. More improvements are needed in the electrolyte tile than in any other single component. For this reason, electrolyte development is receiving special attention at ANL. Characterization of tile properties and the relation of its properties to tile behavior in cells is of major importance. Determination of stability of tile materials is also of high priority.

Operation of cells is required for assessment of the behavior of tiles and other components and for understanding of the performance and life-limiting mechanisms at work within the cell. Cell operation is, of course, coupled with a diagnostic effort and a materials-development effort, with the aim of developing cells of adequate performance and longevity for realistic component testing.

II. ELECTROLYTE DEVELOPMENT

A. Preparation and Characterization of Lithium Aluminate

1. Introduction

The present molten-carbonate fuel cell configuration uses a nonconductive, inert ceramic matrix of lithium aluminate (LiAlO_2) particles to contain the carbonate electrolyte between the anode and the cathode. The use of LiAlO_2 as an electrolyte matrix for the molten-carbonate fuel cell was probably first considered in the middle of the last decade,¹⁻³ but the optimum morphology of the aluminate necessary for long-term fuel cell applications is still unresolved. In this regard, an experimental study was undertaken to prepare homogeneous, finely divided LiAlO_2 which can be developed into the electrolyte matrix for the molten carbonate fuel cell. Various procedures for preparing LiAlO_2 powders with defined particle morphologies were considered in this study.

LiAlO_2 has been prepared by a variety of methods. Generally, physical mixtures of Al_2O_3 and Li_2CO_3 ⁴⁻¹⁰ or oxides of lithium¹¹⁻¹⁵ are heated in air for prolonged periods at 370 to $>1000^\circ\text{C}$ to form LiAlO_2 . Another approach has been to form the aluminate in an aqueous solution. Lileev *et al.*¹⁶ prepared LiAlO_2 (identified by X-ray) by the reaction of $\text{LiAl}_2(\text{OH})_7$ and NaOH in a solution at 90°C . Horan and Damiano¹⁷ reported the formation of LiAlO_2 by precipitation from a Li^+ and Al^{+3} salt solution using NH_3 ; however, no X-ray analysis was performed and the aluminate composition was determined by chemical analysis.

2. Experimental

Two distinct classes of procedures were examined to prepare LiAlO_2 . One class involves the formation of LiAlO_2 by the reaction of Al_2O_3 with Li_2CO_3 - K_2CO_3 mixtures:

The K_2CO_3 and excess Li_2CO_3 were added to the mixture to yield the desired final composition that could be hot-pressed to make an electrolyte structure (tile).

The second class yields LiAlO_2 by the reaction of LiOH and Al_2O_3 :

This preparative procedure was tested with stoichiometric amounts of LiOH only, as well as with excess Li_2CO_3 - K_2CO_3 or excess LiOH - KOH present.

The samples containing Li_2CO_3 and K_2CO_3 in the initial reaction mixture with Al_2O_3 were physically mixed by ball milling. The samples containing the reaction mixture of Al_2O_3 with LiOH or LiOH - KOH were prepared by an impregnation technique. In this impregnation method, the Al_2O_3 powder was added to water and stirred until a uniform slurry was obtained. The hydroxides were dissolved in water and added to the Al_2O_3 slurry, and the resulting mixture was heated on a hot plate or in an oven until the water was evaporated. In this fashion, the alkali hydroxides were impregnated into the porous Al_2O_3 structure during the slow evaporation of water.

The LiAlO_2 produced by Reaction 1 was generally heat-treated at $>600^\circ\text{C}$ in CO_2 , whereas the LiAlO_2 produced by Reaction 2 was generally heat-treated in air at 450 or 600°C . Samples prepared from $\text{KOH-LiOH-Al}_2\text{O}_3$ were also treated by passing CO_2 over the dried, impregnated sample at low temperature (23 – 150°C) to convert the hydroxides to the carbonates. The heat produced by the reaction between CO_2 and the alkali hydroxides was sufficient to cause reaction of LiOH and $\gamma\text{-Al}_2\text{O}_3$, producing LiAlO_2 . After the low-temperature heat treatment in CO_2 , the temperature was increased to 600°C to ensure the complete conversion of hydroxides to carbonates and of Al_2O_3 to LiAlO_2 . These samples contained excess LiOH-KOH in sufficient amounts to yield an electrolyte, after conversion to carbonates, that was of the desired composition for use in the molten carbonate fuel cell.

Thermal gravimetric analyses (TGA) were conducted on samples containing LiOH and Al_2O_3 to determine the kinetics of Reaction 2 in flowing air using an Ainsworth balance. X-ray diffraction analysis* and scanning electron microscopy were used to determine the phases and morphologies, respectively, of the LiAlO_2 particles. Before examining the LiAlO_2 powders, the carbonate salts were removed in an acetic acid/acetic anhydride (80/20 volume ratio) solution, and the remaining LiAlO_2 was washed with absolute methanol.

Alumina obtained from two sources was used. The physical properties quoted by the manufacturers are listed in Table 1. Reagent-grade alkali hydroxides and carbonates were vacuum-dried prior to use.

Table 1. Physical Properties of Alumina

Manufacturer	Type	Phase	Alumina Property	
			Surface Area, m^2/g	Nominal Particle Size, μm
Union Carbide ^a	0.05B	85% $\gamma\text{-Al}_2\text{O}_3$, 15% $\alpha\text{-Al}_2\text{O}_3$	75-90	0.05
	0.3A	90% $\alpha\text{-Al}_2\text{O}_3$, 10% $\gamma\text{-Al}_2\text{O}_3$	6-18	0.3
	1.0C	100% $\alpha\text{-Al}_2\text{O}_3$	1.8-3.0	0.6
Degussa ^b	C	$\gamma\text{-Al}_2\text{O}_3$ (major), $\delta\text{-Al}_2\text{O}_3$ (minor)	100 ± 15	0.02

^aCrystal Products Department, San Diego, CA

^bPigments Division, Teterboro, NJ

*All X-ray analyses discussed in this report were performed by B. S. Tani, Analytical Chemistry Laboratory, Argonne National Laboratory.

3. Results and Discussion

Figure 1 shows the TGA curves for samples prepared by impregnating $\gamma\text{-Al}_2\text{O}_3$ with LiOH or by ball milling a physical mixture of $\gamma\text{-Al}_2\text{O}_3$, LiOH, Li_2CO_3 and K_2CO_3 . The percent weight loss was calculated from the ratio of the measured weight loss on the microbalance and the initial weights of LiOH and Al_2O_3 in the samples. The weight loss for the physical mixtures was in reasonable agreement with the theoretical weight loss of 12.0% for Reaction 2. These results indicate that the reaction between $\gamma\text{-Al}_2\text{O}_3$ and LiOH goes to completion at temperatures less than about 450°C in air. The sample prepared by the impregnation method exhibited a larger percent weight loss than the physical mixture due to the loss of absorbed water. This is not surprising since the impregnated sample was prepared in an aqueous medium, and during the evaporation step, the sample was heated at temperatures ($100\text{--}130^\circ\text{C}$) which were too low to drive off all the absorbed H_2O . These low temperatures were used to prevent the formation of LiAlO_2 during the drying step. Also plotted in Fig. 1 is a TGA curve for the reaction between $\gamma\text{-Al}_2\text{O}_3$ and Li_2CO_3 obtained by Gal *et al.*¹⁰ It is evident that a much higher temperature is necessary to form LiAlO_2 when the starting material is Li_2CO_3 rather than LiOH. In fact,

Fig. 1. TGA Curves for Physical Mixtures of $\gamma\text{-Al}_2\text{O}_3$ with LiOH, Li_2CO_3 , and K_2CO_3 (air, $10^\circ\text{C}/\text{min}$)

- A. $\gamma\text{-Al}_2\text{O}_3 + 2\text{LiOH}$
- B. $\gamma\text{-Al}_2\text{O}_3 + 2\text{LiOH} + 0.7\text{Li}_2\text{CO}_3 + 0.7\text{K}_2\text{CO}_3$
- C. $\gamma\text{-Al}_2\text{O}_3 + \text{Li}_2\text{CO}_3$, Ref. 10.

Gal *et al.* reported that the chemical reaction between Li_2CO_3 and $\gamma\text{-Al}_2\text{O}_3$ was initiated at about 500°C . Belyaev and Annopol'skii⁴ also observed that the reaction between Li_2CO_3 and Al_2O_3 started at about 500°C , whereas the LiOH and Al_2O_3 mixtures reacted at 320°C .

Table 2 summarizes the results obtained from the reaction of physical mixtures of Li_2CO_3 and Al_2O_3 (in the presence of excess $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$) at reaction temperatures of $600\text{--}700^\circ\text{C}$ in flowing CO_2 . After heating at 600°C for short times (24–48 hr), $\alpha\text{-LiAlO}_2$ is the only phase observed by X-ray diffraction analysis, while at longer times (90 hr), minor amounts of $\gamma\text{-LiAlO}_2$ are present. As the reaction temperature increases, the amount of $\gamma\text{-LiAlO}_2$ also increases, as would be expected, since $\gamma\text{-LiAlO}_2$ is the stable phase at high temperatures.^{7,8,10} In all the physical mixtures of Li_2CO_3 and Al_2O_3 reacted at $600\text{--}700^\circ\text{C}$, we have observed that $\beta\text{-LiAlO}_2$ appears in only minor amounts. On the other hand, the reaction between Al_2O_3 and LiOH produces $\beta\text{-LiAlO}_2$ as the major aluminate phase if the reaction temperature is 450°C or lower.

Table 2. Preparation of LiAlO_2 in a Carbonate Medium.

Final Carbonate Composition, $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$	Reaction Temperature, $^\circ\text{C}$	Reaction Time, hr	LiAlO_2 Phases
0.62/0.38 ^a	600	24	$\alpha\text{-LiAlO}_2$
0.62/0.38 ^b	600	51	$\alpha\text{-LiAlO}_2$
0.62/0.38 ^a	600	90	$\alpha\text{-LiAlO}_2$ (major) $\gamma\text{-LiAlO}_2$ (minor)
1/1 ^b	630	115	$\alpha\text{-LiAlO}_2$ (major) $\beta\text{-LiAlO}_2$ (minor)
1/1 ^b	670	24	$\alpha\text{-LiAlO}_2$ (major) $\beta\text{-LiAlO}_2$ (minor) $\gamma\text{-LiAlO}_2$ (very minor)
1/1 ^b	700	19	$\alpha\text{-LiAlO}_2$ (major) $\gamma\text{-LiAlO}_2$ (major) $\beta\text{-LiAlO}_2$ (minor)

^a $\gamma\text{-Al}_2\text{O}_3$ major, $\delta\text{-Al}_2\text{O}_3$ minor (Degussa).

^b 85% $\gamma\text{-Al}_2\text{O}_3$, 15% $\alpha\text{-Al}_2\text{O}_3$ (Union Carbide).

The preparation of LiAlO_2 from LiOH and Al_2O_3 was examined at 450 and 600°C (see Table 3) using the samples of Al_2O_3 listed in Table 1. X-ray diffraction analysis of the products clearly indicated that the allotropic form and/or the particle size of the alumina has a strong influence on which LiAlO_2 phase is formed by the reaction between LiOH and Al_2O_3 at 450°C in air. The alumina samples containing predominantly $\gamma\text{-Al}_2\text{O}_3$ of small particle size yielded $\beta\text{-LiAlO}_2$, while $\gamma\text{-LiAlO}_2$ was the major phase when the starting material was $\alpha\text{-Al}_2\text{O}_3$. When the reaction temperature was increased to 600°C , $\gamma\text{-LiAlO}_2$ was the major phase for all Al_2O_3 starting materials.

Table 3. Effects of Temperature and Al_2O_3 Properties on the Allotropic Form of LiAlO_2 (LiAlO_2 produced by reaction of Al_2O_3 with LiOH)

Al_2O_3 Property		Reaction Temperature, ^a °C	LiAlO_2 Phase
Particle Size, μm	Phase Content, %		
0.05	85 $\gamma\text{-Al}_2\text{O}_3$, 15 $\alpha\text{-Al}_2\text{O}_3$	450	$\beta\text{-LiAlO}_2$
		600	$\gamma\text{-LiAlO}_2$ (major), $\beta\text{-LiAlO}_2$ (medium)
0.3	90 $\alpha\text{-Al}_2\text{O}_3$, 10 $\gamma\text{-Al}_2\text{O}_3$	450	$\beta\text{-LiAlO}_2$ (major), $\gamma\text{-LiAlO}_2$ (minor)
		600	$\gamma\text{-LiAlO}_2$ (major), $\beta\text{-LiAlO}_2$ (minor)
0.6	100 $\alpha\text{-Al}_2\text{O}_3$	450	$\gamma\text{-LiAlO}_2$ (major), $\beta\text{-LiAlO}_2$ (minor)
		600	$\gamma\text{-LiAlO}_2$
0.02	major $\gamma\text{-Al}_2\text{O}_3$, minor $\delta\text{-Al}_2\text{O}_3$	450	$\beta\text{-LiAlO}_2$

^a90 min at reaction temperature in air.

To the best of our knowledge there are no publications, other than those of Fischer,¹² and Chang and Margrave,¹⁵ on the preparation of β -LiAlO₂. Perhaps this is due to the rather restricted experimental conditions under which β -LiAlO₂ is formed. Chang and Margrave synthesized β -LiAlO₂ by reacting Li₂O₂ and Al₂O₃ for 10 hr at a pressure of 18 kbar and 370°C. On the other hand, mixtures of LiOH and Al₂O₃ form β -LiAlO₂ at ambient pressures and <500°C according to the present study and observations by Fischer. It is possible, therefore, that workers previous to Chang and Margrave did not identify β -LiAlO₂ in X-ray diffraction patterns, because its existence was not known.

Although extensive studies have been conducted on the preparation of LiAlO₂ powders,^{4,5,10-12} little information is available on LiAlO₂ particle morphology. Since the electrolyte in the molten carbonate fuel cell is contained within the porous LiAlO₂ matrix, the LiAlO₂ particle morphology is a significant parameter for this technological application. In this regard, the scanning electron microscope has been very useful in examining the morphology of LiAlO₂ particles.

The LiAlO₂ powders prepared by reaction of Al₂O₃ with Li₂CO₃ or LiOH were observed by scanning electron microscopy to have three distinguishable particle morphologies, which are classified as clumps, platelets, and rods. Examples of these particle morphologies are shown in the scanning electron micrographs in Figs. 2-4, respectively. The LiAlO₂ particles classified as clumps appear as agglomerated clusters, as shown in Fig. 2, or as somewhat spherical particles. This particle morphology was evident in both α - and β -LiAlO₂ powders, produced by Reactions 1 and 2, respectively. The LiAlO₂

Fig. 2. Scanning Electron Micrograph of Clump Morphology of α -LiAlO₂

Fig. 3. Scanning Electron Micrograph of Platelet Morphology of β -LiAlO₂

Fig. 4. Scanning Electron Micrograph of Rod-Like Morphology of β -LiAlO₂

particles with platelet morphology are about 4 μm in diameter and $<0.5 \mu\text{m}$ thick. Both α - and β - LiAlO_2 have been observed with this particle morphology, although the reaction conditions were vastly different for the preparation of the aluminates. The α - LiAlO_2 was prepared by heating physical mixtures of γ - Al_2O_3 , Li_2CO_3 , and K_2CO_3 at 600°C in CO_2 for >24 hr, whereas the β - LiAlO_2 was prepared by heating γ - Al_2O_3 impregnated with LiOH at 450°C in air for 1.5 hr.

The rod-like morphology has been observed only with the β - LiAlO_2 allotrope. The rod-like structure in Fig. 4 has a diameter of about $0.7 \mu\text{m}$ and a length of about $4 \mu\text{m}$. The experimental conditions required to produce a rod-like structure with a larger aspect ratio (length/diameter) have not been optimized. Beta-lithium aluminate with a rod-like structure has been produced from LiOH - and KOH -impregnated γ - Al_2O_3 during the reaction of the alkali hydroxides with CO_2 (see Fig. 5). Apparently the heat produced by the reaction to form carbonates is sufficient to raise the sample temperature (usually at $<100^\circ\text{C}$) so that LiOH and γ - Al_2O_3 react to form β - LiAlO_2 . When the sample was heated further at 600°C in CO_2 for 17 hr no noticeable change occurred in the aspect ratio of the β - LiAlO_2 rods (see Fig. 6).

The rod-like structure associated with β - LiAlO_2 has also been obtained in those samples where LiOH and KOH were impregnated into γ - Al_2O_3 (Degussa) and heated in air at 450°C . The experimental conditions used to obtain β - LiAlO_2 by reacting Al_2O_3 with LiOH are summarized in Table 4. When KOH was absent, the β - LiAlO_2 was generally observed to consist of particles with a platelet morphology. It is not clear why the rod-shaped β - LiAlO_2 particles are formed only when KOH is present in the reaction mixture. One explanation may be that KOH and LiOH form a liquidus at the reaction temperature required to form β - LiAlO_2 and the growth of the rod-like structure is facilitated in the presence of a liquid phase.

The experimental results on the synthesis of LiAlO_2 may be summarized as follows:

- (1) The allotropic form of LiAlO_2 produced from LiOH is dependent on the type of Al_2O_3 (α - or γ - Al_2O_3) and the reaction temperature.
- (2) β - LiAlO_2 is the major phase formed by the reaction of LiOH and γ - Al_2O_3 at 450°C or lower.
- (3) α - LiAlO_2 is not formed by reaction of LiOH and Al_2O_3 .
- (4) α - LiAlO_2 is the major phase formed by the reaction of Li_2CO_3 and γ - Al_2O_3 at 600 - 700°C .
- (5) β - LiAlO_2 was produced with morphologies classified as rods, platelets and clumps, whereas α - LiAlO_2 was produced only as platelets and clumps.

Fig. 5. Scanning Electron Micrograph of β -LiAlO₂
Obtained from LiOH-KOH-Al₂O₃ Heated at 100°C
for 2 hr in CO₂

Fig. 6. Scanning Electron Micrograph of β -LiAlO₂
Heated at 600°C in CO₂ for 17 hr in the
Presence of Li₂CO₃-K₂CO₃

Table 4. Preparation of LiAlO_2^a in a Hydroxide Medium

Hydroxide Composition	Gas Environment	Time, hr	Reaction Temperature, °C	LiAlO ₂ Property	
				Phase	Morphology
LiOH	Air	1.5	450	β -LiAlO ₂	platelets, clumps
LiOH + KOH	Air	1.5	450	β -LiAlO ₂	rods
LiOH + KOH	CO ₂	2-19	23 or 100	β -LiAlO ₂	rods

^aLiAlO₂ formed by reaction of LiOH and γ -Al₂O₃.

B. Phase and Structural Stability of LiAlO₂

1. Introduction

The electrolyte in the molten carbonate fuel cell is contained within the porous structure of the LiAlO₂ particles. For successful long-term performance of the molten carbonate fuel cell, the LiAlO₂ structure must give up some of the electrolyte to the adjacent porous anode and cathode but not in sufficient quantities to flood the porous electrodes. This balance in the amount of electrolyte in the porous electrodes and in the LiAlO₂ matrix is governed by the pore size distribution of the three porous structures as discussed by Maru and Marianowski.¹⁸ Achieving the proper distribution requires control of the phase and dimensional stability of the LiAlO₂ particles at operating fuel cell conditions and life times. The LiAlO₂ particle shape, allotropic form, and weight fraction also control tile conductivity. (A discussion of these factors is given in the Appendix.) We have therefore initiated experiments to study the stability of the various allotropic forms of LiAlO₂ in the presence of molten carbonates at 600-700°C. The LiAlO₂ particles are examined by scanning electron microscopy to follow any changes in the particle morphology, and by X-ray diffraction to follow changes in allotropic form.

The three allotropic forms of LiAlO₂, α , β and γ , have densities of 3.401,¹⁹ 2.61,¹² and 2.615²⁰ g/cm³, respectively. Thus, a phase transformation from α -LiAlO₂ to β - or γ -LiAlO₂ in the electrolyte matrix produces a volume change in the LiAlO₂ which might be detrimental to fuel cell performance. In addition, a change in the morphology of LiAlO₂ particles during fuel cell operation might also adversely affect cell performance by altering the pore structure of the LiAlO₂ matrix.

2. Experimental

The stability studies were conducted with powder mixtures of LiAlO₂, Li₂CO₃, and K₂CO₃ and with electrolyte tiles which were tested in a molten carbonate fuel cell. The powder samples were heated in gold crucibles at 700°C in an environment of flowing CO₂. Similar tests are under way at 650°C. The electrolyte tiles were tested in a 2 3/4-in.-dia fuel cell at 600-675°C with 80% H₂/20% CO₂ in the anode and 60% CO₂/30% O₂/10% Ar in the cathode. After testing, all samples were ground with a mortar and pestle and then placed in

a 80/20 vol % acetic acid/acetic anhydride solution to dissolve the carbonate salts. The carbonate-free LiAlO_2 was then examined by X-ray diffraction and scanning electron microscopy to determine the phases and particle morphologies, respectively.

3. Results and Discussion

The results obtained on the phase stability of LiAlO_2 in the presence of molten $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ at 650-700°C are summarized in Table 5. These results indicate that both α - and β - LiAlO_2 undergo phase transformation to γ - LiAlO_2 . There is no evidence to suggest that α - LiAlO_2 transforms to β - LiAlO_2 or vice-versa under the experimental conditions outlined in Table 5; however, there is ample evidence in the published literature showing that α - LiAlO_2 transforms to γ - LiAlO_2 at >600°C.^{5,7,8,10,21} Our results are not yet sufficient to reach any conclusion as to the effects of different molten carbonate compositions on the phase stability of LiAlO_2 . At 700°C in a CO_2 environment β - LiAlO_2 undergoes phase transformation to γ - LiAlO_2 in less than 100 hr. In contrast, Chang and Margrave¹⁵ observed no phase transformation upon heating β - LiAlO_2 in platinum crucibles at 710°C for 3 days. However, this experiment was performed on β - LiAlO_2 in the absence of a molten salt.

In molten carbonate fuel cells, α - LiAlO_2 in the electrolyte matrix opposite the electrodes was unchanged after operation at 675°C for 100 hr or at 650°C for 625 hr. However, α - LiAlO_2 in the wet-seal area appeared to undergo phase transformation to γ - LiAlO_2 . This difference in the phase stability of α - LiAlO_2 , depending on the location in the molten carbonate fuel cell, can be due to several causes. Semenov²¹ reported that α - LiAlO_2 mixed with Li_2CO_3 transformed more rapidly to γ - LiAlO_2 at 700-800°C as the amount of Li_2CO_3 increased (English translation, "mineralizing effect"). This observation suggests the possibility that the transformation of α - LiAlO_2 in the fuel cell may be dependent on the amount of molten carbonate salt mixed with the LiAlO_2 matrix. Visual examination of the fuel cell anode and cathode housing clearly showed the presence of a white salt film adjacent to the wet seal. X-ray analysis of the salt film indicated the major phase was Li_2CO_3 with K_2CO_3 as a minor phase. Atomic absorption measurements confirmed the X-ray results, indicating the presence of 96 wt % Li_2CO_3 and 3 wt % K_2CO_3 . Chemical analysis of the lithium and potassium content of the electrolyte tile ($\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3/\text{LiAlO}_2$) samples taken in the wet-seal area and in the region opposite the electrodes showed no significant differences in concentration. Based on the few chemical analysis for lithium and potassium content of the electrolyte tile, the "mineralizing" effect reported by Semenov does not appear to explain the phase transformation from α - LiAlO_2 to γ - LiAlO_2 in the wet seal of the electrolyte tile. An alternative explanation for the phase transformation of α - LiAlO_2 to γ - LiAlO_2 in the wet-seal area of the molten carbonate fuel cell may be in the availability of CO_2 (or other gaseous species) in this region of the electrolyte tile. Gal *et al.*¹⁰ observed that α - LiAlO_2 was transformed to γ - LiAlO_2 at a lower temperature in air ($\sim 850^\circ\text{C}$) than in carbon dioxide ($\sim 950^\circ\text{C}$). Thus, a lack of CO_2 in the wet seal may cause the α - LiAlO_2 in this area of the electrolyte tile to transform more rapidly to γ - LiAlO_2 than the α - LiAlO_2 in contact with CO_2 in the electrolyte tile opposite the porous fuel cell electrodes. Further analyses of electrolyte tiles from operational molten carbonate fuel cells are necessary to determine whether the results obtained with fuel cell KK7 are typical of long-term operation.

Table 5. Phase Stability of LiAlO_2 in a $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ Medium^a

Initial LiAlO_2 Phase	Environment	Temperature, °C	Time, hr	Final LiAlO_2 Phase
$\alpha\text{-LiAlO}_2^b$	Electrolyte matrix opposite electrodes in Cell JS1	675	100	$\alpha\text{-LiAlO}_2$
$\beta\text{-LiAlO}_2^b$	CO_2	700	24	$\beta\text{-LiAlO}_2$
$\beta\text{-LiAlO}_2^c$	CO_2	700	26	$\beta\text{-LiAlO}_2$ (major) $\gamma\text{-LiAlO}_2$ (minor)
$\beta\text{-LiAlO}_2^c$	CO_2	700	100	$\gamma\text{-LiAlO}_2$
$\beta\text{-LiAlO}_2$ ($\alpha\text{-LiAlO}_2$, minor) ^c	CO_2	700	67	$\gamma\text{-LiAlO}_2$ (major), traces of $\alpha\text{-}$ and $\beta\text{-LiAlO}_2$ possible
$\alpha\text{-LiAlO}_2^c$	Electrolyte matrix opposite electrodes in Cell KK7	650	625	$\alpha\text{-LiAlO}_2$
$\alpha\text{-LiAlO}_2^c$	Electrolyte matrix in wet seal in Cell KK7	650	625	$\gamma\text{-LiAlO}_2$ (major) $\alpha\text{-LiAlO}_2$ (minor)

^a55 wt % liquid phase.

^b $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$, 1/1 mole ratio.

^c $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$, 0.62/0.38 mole ratio.

Beta lithium aluminate particles with a rod-shaped morphology (Fig. 4) were heated at 700°C for 26 and 100 hr in CO₂ and then examined by scanning electron microscopy and X-ray diffraction analysis. After heat treatment for 26 hr, only a minor amount of β -LiAlO₂ transformed to γ -LiAlO₂ and no significant change occurred in the LiAlO₂ particle morphology (see Fig. 7). After 100 hr, however, β -LiAlO₂ transformed completely to γ -LiAlO₂ with a bipyramidal structure (Fig. 8). Another experiment indicated that β -LiAlO₂ with a platelet morphology heated to 700°C for 24 hr (see Table 5) in CO₂ remained as β -LiAlO₂ and showed no observable change in particle morphology.

Scanning electron microscopy of LiAlO₂ from the electrolyte tile of Cell KK7 showed that distinct changes in particle morphology accompanied phase transformation. In the area opposite the porous electrodes, the α -LiAlO₂ (see Fig. 9) appears to have retained the original morphology, namely, the clump morphology shown in Fig. 2, although close examination of Fig. 9 shows evidence for the presence of some small bipyramidal particles. However, the particles from the wet seal area, which had been transformed to γ -LiAlO₂ exhibited a bipyramidal structure (see Fig. 10) similar to the γ -LiAlO₂ structure in Fig. 8.

The study of the phase and structural stability of LiAlO₂ under conditions simulating fuel cell operation will be continued, along with post-test analyses of LiAlO₂ from our cell tests.

Fig. 7. Scanning Electron Micrograph of β -LiAlO₂ Heated in CO₂ and Carbonate at 700°C for 26 hr

Fig. 8. Scanning Electron Micrograph of β -LiAlO₂ Heated in CO₂ and Carbonate at 700°C for 100 hr

Fig. 9. Scanning Electron Micrograph of α -LiAlO₂ from Center of Tile, Cell KK-7

C. Pressing of Electrolyte Tiles

Powdered mixtures of Li_2CO_3 , K_2CO_3 , and LiAlO_2 of the desired composition are formed into tiles by hot-pressing at $\sim 10^\circ\text{C}$ below the liquidus temperature ($\sim 500^\circ\text{C}$) of the carbonate mixture. The tile is pressed at 46,000 kPa (6700 psi) for 30 min and then the pressure is released before cooling. Lower pressures or temperatures and shorter times may be adequate, but these conditions yield crack-free tiles of approximately theoretical density.

The die is a simple cylinder of 6.98 cm (2 3/4 in.) ID, 12.7 cm (5 in.) OD and 3.81 cm (1 1/2 in.) depth. The powder is compressed between rams which are approximately 0.00127–0.0025 cm (0.0005–0.0010 in.) smaller in diameter than the die body. All parts are made of hardened and ground H-21 steel, and are coated by spraying with graphite lubricant before use. Heat is provided by stainless steel platens above and below the die, each of which is bored for five 1.27-cm (1/2-in.)-dia heater cartridges. The entire platen and die assembly is wrapped with 2.54 cm (1.0 in.) of insulating batting prior to heating.

The powdered electrolyte/ LiAlO_2 mixture is ground or ball-milled and then passed through a 170 mesh (90 μm opening) sieve prior to loading in the die. The powder is leveled in the die with a close-fitting blade. The loading step is fairly critical, since uneven powder distribution is believed to cause uneven thickness of the finished tile. Tiles produced to date are typically 0.220 ± 0.008 cm (0.085 ± 0.003 in.) thick; special care is required to maintain closer thickness tolerances. The effect of finer grinding of powders (-325 mesh) on uniformity of thickness is under investigation.

III. CELL TESTING

The primary objective of ANL cell testing is to evaluate cell components at the present time, especially the electrolyte tile, and to understand and control the changes which occur in the components during cell operation. Although optimization of cell design is not a primary objective, efforts are made to improve cell performance and cell lifetime, so as to operate the components under conditions representative of realistic, state-of-the-art cells. Stable performance for long-term testing is more important in meeting the primary objective than is maximum powder density.

The changes observed in the LiAlO_2 phase and particle morphology during cell operation are discussed in the preceding sections. This section is concerned with cell construction, polarization data, and long-term performance of some of the laboratory cells.

A. Cell Construction

To date, ten cells have been operated. With the exception of the very first cell (JS-1, a rectangular cell with reference electrode) all cells had the configuration illustrated in Fig. 11. The housings were circular, 6.98-cm (2.75-in.) OD, with a 0.64-cm (0.25-in.)-wide wet-seal area around the perimeter. The depth of the electrode compartments was 0.24 cm (0.093 in.). The current collectors were Type 316 stainless steel perforated sheets, 0.089 cm (0.035 in.) thick, with an open space of 36%. The only modifications of this configuration to date have been in the support structures for the current collectors. Electrodes were identical for all cells except the most recent one, Cell KK-8, in which the usual anode material was precompressed from 0.053 cm (0.021 in.) to 0.033 cm (0.013 in.) thick. The major parameter that was varied from cell to cell was the electrolyte tile (its carbonate content and method of LiAlO_2 preparation). Important parameters of cell construction are summarized in Tables 6 and 7.

Fig. 11. Construction of Cell with Nonintegral Current Collector Support

Table 6. Fixed Parameters of Cell Construction^a

	Thickness, cm	Porosity, %	Mean Pore Size, μm	Open Space, %
Anode	0.053	65	8	--
Cathode	0.076	75	12	--
Current Collectors, both electrodes	0.089	--	--	36

^aFuel composition: 80% H_2 , 20% CO_2 , saturated at 25°C with H_2O .

Oxidant composition: 30% O_2 , 60% CO_2 , 10% Ar.

Geometric electrode areas: 25.6 cm^2 .

Electrode compartment depth: 0.24 cm (0.093 in.).

Table 7. Variable Parameters of Cell Tilco

Cell No.	Thickness, cm	LiAlO_2 Preparation Method ^a	LiAlO_2 Phase	Liquid-Phase Content of Tile, wt % Alkali Carbonates	Liquid-Phase Composition, Li_2CO_3 - K_2CO_3 , mol %
JS-1	0.20-0.21	Molten Salt	α	55	50/50
KK-1	0.20-0.22	Molten Salt	α	50	50/50
KK-2	0.21-0.23	Molten Salt	α	50	62/38
KK-3	0.21	Molten Salt	α	50	62/38
KK-4	0.21-0.24	Molten Salt	α	50	50/50
KK-5	0.23-0.24	Aqueous LiOH	β (major) α (minor)	55	62/38
KK-6	0.25-0.26	Aqueous LiOH	β (major) α (minor)	55	62/38
KK-7	0.20	Molten Salt	α	55	62/38
KK-8	0.20-0.21	Molten Salt	α (major) γ (minor)	55	62/38

^aSee Section II.A for description of methods.

Cells of this configuration were assembled in the test stand illustrated in Fig. 12. Pressure was applied to the cell through the pressure pedestals, which also contained the heaters. Ceramic insulators were placed between the pedestals and the cell housings to prevent short circuiting or grounding of the cell. Fuel and oxidant gases were supplied by separate lines, and in later cells (KK-7 and KK-8), the gases were preheated before they entered the cell. The inlet flow rates were monitored continuously with a mass flowmeter (anode) and rotameters (anode and cathode). The effluent flow rates were monitored intermittently, at open circuit, to determine the wet

Fig. 12. Cell Assembly in Test Stand

seal efficiency. Separate current and voltage leads were attached to the gas supply tubing, which had been welded to the cell housings.

In early cells various spacers were used to set the height of protrusion of the electrodes above the cell housing. The spacers did not provide adequate control of this parameter, or adequate current collector support; therefore, the cell design shown in Fig. 13 has been adopted.

Fig. 13. Construction of Cell with Integral Current Collector Support

B. Cell Operation

Heating rates during cell startup were $\sim 2^\circ\text{C}/\text{min}$. The holding pressure applied to the cell was varied from ~ 34.5 kPa to ~ 64.0 kPa (~ 5 to ~ 90 psi). In general, if the cell developed a gas leak around the wet-seal area, increasing the holding pressure did not eliminate the leak. At the higher end of the holding pressure range, damage to the electrodes and other cell components was observed. Thus, the desired mode of operation is with a minimum holding pressure consistent with leak-free operation.

Performance of the cells was generally tested by measuring voltage as a function of current density, while maintaining constant gas flow rates. The data in Figs. 14-17 were obtained in this manner. An anode flow rate of 9.5 std. cm^3/min ($80\% \text{H}_2$, $20\% \text{CO}_2$) was taken as the equivalent of 1 A of H_2 fuel. A cathode flow rate of 12.7 std. cm^3/min ($30\% \text{O}_2$, $60\% \text{CO}_2$, $10\% \text{Ar}$) was taken as the equivalent of 1 A of oxidant gas. Thus, in Figs. 14-17, when the flow rates to both electrodes are 3 A and the cell under load is delivering x A of current, the current density is $x/25.6$ cm^2 , and the percent utilization of both fuel and oxidant is $(x/3) \cdot 100$. Another method used in testing the cells was to measure voltage as a function of current density at constant conversion. To obtain this type of data, the current drawn from the cell and the flow rate of the anode gas to the cell were varied simultaneously so as to maintain a constant fuel utilization (as defined above). The cathode flow rate was maintained at a constant rate so that oxidant utilization was negligible. Data for Cell KK-7, obtained in this manner, are shown in Fig. 18.

The cell resistances reported in Figs. 14-17 were measured by the current interruption technique.²² With the cell under load, the circuit was opened instantaneously (by a mercury relay switch), and the decay of the overpotential with time was recorded on an oscilloscope and stored in a waveform recorder for later printout. The ohmic or resistive overpotential decays much more rapidly than other types of overpotential; thus, its magnitude was measured as the initial vertical portion of the overpotential decay curve.

Fig. 14. Cell Performance vs. Amount of Liquid Phase in the Electrolyte
 Anode gas: 80% H₂, 20% CO₂ sat'd. with H₂O at 25°C
 Cathode gas: 30% O₂, 60% CO₂, 10% Ar
 Electrode area: 25.6 cm²
 Temperature: 650°C
 Flow rates: 3 A (to both electrodes)

Fig. 15.

Performance of Cell KK-4 vs. Time of Operation

Anode gas: 80% H₂, 20% CO₂ sat'd. with H₂O at 25°C

Cathode gas: 30% O₂, 60% CO₂, 10% Ar

Electrode area: 25.6 cm²

Temperature: 650°C

Flow rates: 3 A (to both electrodes)

Fig. 16. Comparison of IR-Free Voltages for Cells KK-5 and KK-8
 Anode gas: 80% H₂, 20% CO₂ sat'd. with H₂O at 25°C
 Cathode gas: 30% O₂, 60% CO₂, 10% Ar
 Electrode area: 25.6 cm²
 Temperature: 650°C
 Flow rates: 3 A (to both electrodes)

Fig. 17. Life Graph of Cell KK-7 (temperature, 650°C; 3 A flow to both electrodes)

1. 30 mA/cm², 25.7% utilization
2. 50 mA/cm², 42.7% utilization
3. 70 mA/cm², 59.8% utilization
4. 100 mA/cm², 85.5% utilization

Fig. 18. Constant Conversion Polarization Data for Cell KK-7
 Temperature: 650°C
 Cathode utilization: 3.7% at 10 mA/cm²,
 37% at 100 mA/cm²
 Cell resistance: 53 mΩ

C. Cell Performance

Performance data are shown in Fig. 14 for cells in which the amount of liquid phase in the electrolyte was varied. On increasing the amount of liquid phase in electrolyte from 50 to 55 wt %, a significant improvement in cell performance was observed; this was attributed to improved wetting of the electrodes. This explanation is supported by post-test measurements of the amount of alkali carbonates in the anodes (see Table 8). For cells with 50 wt % liquid phase in the electrolyte, wetting of the electrodes was gradual and performance improved as wetting proceeded, as can be seen in Fig. 15, where performance data for Cell KK-4 are shown as a function of time in operation. After 160 hr in operation, the measured amount of alkali carbonate in the anode of Cell KK-4 was 5.1 vol. %. A similar cell (KK-3) with 50 wt % liquid phase in the electrolyte had only 2.2 vol % alkali carbonate in the anode after 48 hr of operation. Its performance had been comparable to the initial performance (presumably, before adequate electrode wetting) of Cell KK-4. Thus, the improvement in performance of Cell KK-4 with time appears to be directly correlated with electrode wetting.

For cells with 55 wt % liquid phase in the electrolyte, electrode wetting was more immediate and complete than for cells with 50 wt %. This can be seen in Fig. 14, where initial performance of Cell KK-5 (55 wt %) exceeds the final (and best) performance of Cell KK-4 (50 wt %). The anode of Cell KK-5

Table 8. Cell Operating Parameters

Cell No.	Operating Time, hr	Maximum Temperature, °C	Final ^a Porosity, %	Electrolyte Composition wt % Liquid	Alkali Carbonate Content of Anode, ^b vol %
JS-1	288	675	53	55	5.2
KK-1	24	600	65	50	1.5
KK-2	72	690	--	50	---
KK-3	48	675	65	50	2.2
KK-4	160	690	49	50	5.1
KK-5	145	700	36	55	5.5
KK-6	70	650	--	55	---
KK-7	672	675	--	55	---
KK-8	308	645	--	55	---

^aOriginal porosity, 65%.

^bPost-test measurement.

contained 5.5 vol % alkali carbonate after 145 hr, as compared to 5.1 vol % for Cell KK-4 after 160 hr operation. Thus, the higher amount of liquid phase in the electrolyte of Cell KK-5 promoted wetting of the electrodes, with a resulting increase in performance.

The most recently operated cell, Cell KK-8, had an electrolyte containing 55 wt % liquid phase. Its peak performance was the best obtained (see Fig. 14). However, the improved performance was due more to decreased cell resistance than to improved electrode wetting, as can be seen in Fig. 16, where the IR-free voltage of Cell KK-8 is shown to be lower than that of Cell KK-5. The IR-included voltages for the same cells are shown in Fig. 14, where the opposite relationship exists. Post-test examination of Cell KK-8, however, indicated that a large portion of the anode had separated from the electrolyte. The current collector failed to fully support the anode. Thus, a truly valid evaluation of cell performance cannot be made for Cell KK-8.

One long-term cell test was completed for Cell KK-7. The cell was operated for a total of 672 hr (48 hr of which were involved in thermal cycles). Cell resistance was stable throughout operation. Cell performance was reasonably stable, as shown in Fig. 17, until 350 hr of operation, when the decline in cell voltage accelerated. The thermal cycles to which the cell was subjected did not appear to seriously affect cell performance, which had already been declining. As mentioned in the first section of this report, a change in LiAlO_2 phase and morphology was observed in electrolyte taken from the wet-seal area of this cell. A similar change was not observed in material taken from the electrolyte between the electrodes; however, the conclusion that a correlation exists between cell lifetime and change in the LiAlO_2 particles would be premature at this time.

One additional cell (OH-1), which utilized an electrolyte tile prepared by a novel technique, was also tested. Except for the electrolyte, cell construction was identical to that of the cells described above. The electrolyte consisted of $\gamma\text{-Al}_2\text{O}_3$ (Degussa), which had been impregnated with LiOH and KOH (aqueous solutions), heated at 450°C in air for 2.5 hr to form the LiAlO_2 , and finally hot-pressed at 200°C for 30 min. Conversion of the hydroxides to the carbonates was accomplished *in situ* during starting operation of the cell. The fuel and oxidant gases (see Table 6 for composition) were passed through the cell, at gradually increasing temperatures, in order to accomplish the conversion. Performance data for this cell are shown in Fig. 19. A cross-leak of anode and cathode gases and a gas leak in the wet seal occurred during startup. Although performance was not as good as the most recent ANL cells, the results are superior to performance obtained from the first ANL cells; they are encouraging results for a radically different approach to cell construction.

This approach to electrolyte tile manufacture, in which conversion of the alkali hydroxides to the carbonates occurs in the fuel cell, has some advantages over the conventional approach, and certain disadvantages as well. The major advantage, from a manufacturing point of view, is that preparation of the LiAlO_2 from the hydroxides and the subsequent electrolyte tile pressing operations, are performed at lower temperatures than for the conventional carbonate method. Also, fewer operations are involved in obtaining the final pressable mixture. The major disadvantage, however, involves the difficulty in controlling the tile integrity during the conversion of the hydroxides to the carbonates. Nevertheless, the results from Cell OH-1 (Fig. 19) are promising and further investigations will be made to assess the feasibility of this method of tile construction.

Fig. 19. Performance of Cell OH-1 (gases leaking across electrolyte tile and through wet seal)
 Anode gas: 80% H₂, 20% CO₂
 Cathode gas: 30% O₂, 60% CO₂, 10% Ar
 Temperature: 650°C
 Cell resistance: 40 mΩ

IV. COMPONENT ANALYSIS AND DEVELOPMENT

The objectives of this effort are (1) to analyze and evaluate both short- and long-term behavior of cell components, (2) to select material and fabrication methods for cell components other than the tile, and (3) to develop diagnostics for all cell components. This section of the report is divided into three areas: post-test component analysis, development of tile physical-properties tests, and development of cell housing materials.

A. Post-Test Component Analysis

The purpose of this task is to analyze and evaluate changes which occur in cell components during operation.

1. General

Upon termination of cell operation, a film of electrolyte is usually observed on anode housings near the electrolyte tile. Little or no electrolyte can be observed on the cathode housing, regardless of whether the cells are operated with anode or cathode uppermost. The amount of the film varies greatly from cell to cell, and may be related to differences in the electrolyte structure.

Upon disassembly, the anode wet seal always shows more corrosion than does the cathode, as would be expected because of the difference in gas composition and consequent potential across the seal, and because of the high humidity of the anode gas. Also, during operation the anode wet seal typically leaks 5-15% of the fuel gas passing into the cell, even at very low back pressures (<250 Pa) while cathodes are typically leak free.

The anode inlet lines at the entrance to the cell housing contain carbon if the cells had been operated with 80% H₂/20% CO₂ fuel, although this mixture theoretically cannot be in equilibrium with solid carbon at cell temperatures.^{23,24} The carbon buildup can block small inlet tubes, but saturation of the fuel gas with water at 25°C or above mitigates the problem.

The cathode is always a black, very brittle structure which adheres strongly to the electrolyte tile. The anode is bright and metallic, and is less strongly attached. Cathode current collectors have a thin, black, adherent film; anode current collectors appear to be shiny and metallic, but may show occasional, strong localized corrosion at apparently random locations.

2. Electrolyte Tiles

The tile itself is typically strong and intact between the electrodes, but it is weak, crumbly, and discolored with iron oxide in the wet-seal area. This phenomenon may be due to reaction with the housing and accumulation of corrosion products. Future cells will be protected at the wet-seal area with aluminide or aluminized coatings. The crumbling of the tile may also be caused by the decomposition of the carbonates to oxides at the edge of the tile where the wet seal prevents access of CO₂ to the tile. State-of-the-art cells with protected wet seals apparently do not show tile-strength degradation in the wet-seal area, but do show some accumulation of corrosion products there.²⁵ In Cells KK-7 and KK-8, the α -LiAlO₂ particles in the wet-seal area tended to convert to the γ -LiAlO₂ and seemed to assume a square bipyramidal shape.

Upon cell disassembly, it has been generally observed that cathode material (NiO) adhered to (or was embedded in) the electrolyte tile. Additionally, a diffused, greyish layer appears to have been formed on the cathode side of the tile. We have observed such a layer on the cathode side in tiles of at least four of the seven cells. The thickness of this layer varies from cell to cell and so far does not appear to depend on the duration of operation. Sometimes the nickel anode has been embedded into the tile; however, this did not produce any diffused layer on the anode side.

Figure 20 shows a cross-section of the tile from Cell KK-2, which had been operated for 72 hr. The diffused gray layer is quite apparent in the tile. It was suspected that the diffused layer is formed as a result of NiO diffusion into the tile from the cathode side; therefore, a technique for analyzing this layer for its impurities was developed. This method is being used consistently for analyzing those tiles in which diffused layers are quite apparent.

The technique involves (1) grinding off the adherent NiO from the cathode side of the tile, (2) grinding the anode side up to the diffused layer boundary so that the only diffused material is contained in the remaining carbonate matrix, (3) treating the remaining tile with distilled water (or a 1:4 mixture of acetic anhydride and acetic acid) to leach out the carbonates, and (4) thoroughly washing the insoluble material with methanol and drying at 100°C. The dried substance is then analyzed using X-ray diffraction and a technique (EDXA-SEM) that utilizes the energy-dispersive X-ray capability of the scanning electron microscope. Table 9 gives the results of these analyses to date.

It is apparent that thickness of the diffused layer does not show any relationship to the number of hours the tile was used in a cell. Except on the first tile (KK-2), the diffused layer was no more than 0.25 mm (0.010 in.) thick. X-ray diffraction analysis indicated the possible presence of nickel oxide (NiO) in three of these tiles.

In electrolyte tile KK-4, X-ray diffraction indicated the presence of nickel, which was unexpected. This specimen was analyzed twice to confirm the presence of elemental nickel, not NiO. Since the existence of elemental nickel on the cathode side is thermodynamically questionable, this finding cannot be explained. All the X-ray results were confirmed by scanning cross-sections of the tile using the EDXA-SEM. All the specimens indicated an increased concentration of nickel in the diffused layer over that in the undiffused area of the tile. Figure 21 shows the EDXA scans of fractured specimens of tiles from Cells KK-5 and KK-7. An increase is found in nickel concentration on the cathode sides (diffused layers, Fig. 21c and d) over that in the undiffused area (Fig. 21b, for KK-5). This nickel was suspected to be in the form of NiO from the results of the X-ray diffraction analysis.

The above-mentioned results suggest that some kind of reaction (or simple diffusion) may be occurring on the cathode/tile interface. However, it is difficult to make a conclusive judgement for an operative mechanism. It is likely that forced embedment of cathode onto the molten tile during operation has produced a diffused layer by mere mechanical liquid mixing. Further, the extent of such mixing (diffusion) appears to depend on the matrix of tile rather than time of operation. This investigation will be continued on future cell tiles until the diffused layer anomaly is understood.

a. broken electrolyte tile after 72 hr of operation
(1.5X; black surface is cathode side)

b. cross-section of electrolyte tile
(5X; dark grayish layer is cathode side)

Fig. 20. Tile from Cell KK-2

a. Base without specimen (integrated Ni intensity, ~ 1720)

b. In Tile KK-5 away from diffused layer (integrated Ni intensity, ~ 2350)

c. In diffused layer of Tile KK-5 (integrated Ni intensity, ~ 7985)

d. In diffused layer of Tile KK-7 (integrated Ni intensity, ~ 7430)

Fig. 21. EDXA-SEM Scans for Tiles KK-5 and KK-7

Table 9. Properties of Diffused Layers in Electrolyte Tiles

Tile No.	Cell Operating Time, hr	Original Thickness of Tile, mm	Av. Thickness of Diffused Layer, mm	X-Ray Diffraction		EDXA-SEM Identification
				Minor Phase	Major Phase	
KK-2	72	2.0-2.3	1.1	NiO	α -LiAlO ₂	Ni, Al
KK-4	160	2.1-2.4	0.16	Ni ^a	α -LiAlO ₂	Ni, Al
KK-5	145	2.3-2.4	0.27	NiO ^a	α - and β -LiAlO ₂ ^b	Ni, Al
KK-7	672	2.0	0.22	NiO ^a	α -LiAlO ₂	Ni, Al

^aSuspected. Only two strong lines (NiO or Ni) were indicated; third suspected line could have overlapped with LiAlO₂ pattern.

^b β -LiAlO₂, medium.

3. Cell Housings

During this quarter, an analysis of the anode cell housing of Cell JS-1 was completed. This was the first cell run at ANL, and both its configuration and the extent of corrosion were atypical of later cells. However, it had a very broad, unprotected wet seal, which may be regarded as providing an extreme example of the same kind of wet-seal corrosion seen in later cells. The corroded areas were analyzed to obtain a general interpretation of corrosion mechanisms. The anode part of the housing was severely corroded, especially at the areas where the tile was not in contact with feed gases. The corrosion product was black, hard, and magnetic, and formed a thick (1.5 mm) layer and blisters. As shown in Fig. 22, the electrolyte also had seeped onto the edges of the housing and formed a yellow product. Area Z2 directly opposite the reference electrode (which was located in the cathode housing) was not corroded. In general, the housing was corroded at those regions where anode or cathode gas was not in contact with electrolyte tile. Apparently the carbonates were decomposing to corresponding oxides and the latter were corroding the housing.

Three areas of the anode housing, namely, Z1, Z2, and Z3, shown in Fig. 22, were analyzed using X-ray diffraction, optical microscopy, and EDXA-SEM techniques. Corrosion was negligible or almost absent in the area Z2 (see Fig. 23), while it was quite massive in the areas Z1 and Z3 as shown in Figs. 23 and 24. The scale consisted of four or five different oxide layers, similar to scales that have been observed in the gaseous oxidation of iron and iron base-alloys.²⁶ The region Z1 contained oxides of iron, chromium, and nickel. The various layers apparently contained iron in different oxidation states. The top layer consisted almost entirely of Fe₂O₃, the intermediate layers were a mixture of Fe₂O₃, FeO (or Fe₃O₄), NiO, and chromium oxides, and the layer next to the alloy (Type 316 stainless steel) mainly consisted of FeO, NiO and chromium oxides probably in the form of spinels. The chromium oxide layer, near the alloy/oxide interface, could also be in the form of LiCrO₂, but detection of lithium is not possible with EDXA-SEM methods. The

Fig. 22. Schematic of Cell JS-1 Anode Housing

chromium oxide layer formed a dense barrier layer for further oxidation of alloy. The top scale layer in the Z1 area also indicated a slight concentration of aluminum, which was suspected to be due to inclusion of LiAlO_2 particles in the porous layer of Fe_2O_3 . Somewhat similar results were obtained at the area Z3 except that aluminum was not present in the top layer, and no chromium enrichment was observed in the Fe_3O_4 layer. The analysis at the area Z2 did not indicate any scale formation.

No extensive interpretation of the corrosion mechanisms will be presented until more such analyses have been performed on other cells. The concentration of the chromium oxide layer near the oxide/alloy interface is typically observed in the oxidation of stainless steels.²⁶ The growth of the outer layer of Fe_2O_3 results mainly from the more rapid diffusion of iron, as compared with the other elements. It is also quite likely that in the beginning stages of scale formation (before a thick layer of iron oxide is formed), chromium oxide could be selectively leached out by molten carbonates. This may be the explanation for the X-ray diffraction results that indicated the presence of K_2CrO_4 in yellow deposits obtained from the edges of cell housing. Of course, the Type 316 stainless steel housing was observed to be completely sensitized after 200 hr operation at $\sim 600^\circ\text{C}$ (*i.e.*, grain boundaries indicated a massive precipitation of carbides).

Fig. 23. Photomicrographs of Areas Z1, Z2, and Z3 of Cell JS-1 (100X)

Area Z1
(600X)

← Mainly Fe_2O_3
and Al oxide

← Rich in Cr oxide
(and some Fe_3O_4)

Spinel of FeO ,
 Cr_2O_3 , Fe_2O_3
and NiO

Area Z3
(1500X)

← Mainly Fe_2O_3

← Fe_3O_4

← Spinel of FeO ,
 Cr_2O_3 , Fe_2O_3
and NiO

Fig. 24. Scanning Electron Micrographs
of Areas Z1 and Z2, Cell JS-1

B. Tile Diagnostics

Routine nondestructive diagnostics include measurement of uniformity of thickness (typically, ± 0.1 mm) and determination of as-pressed density (usually within 1-2% of theoretical). Although X-radiography is a sensitive tool for detecting cracks, the tiles apparently are always either sound or contain large enough cracks for observation with a low-power microscope. The latter technique is used routinely.

Tile samples sent to Harrop Laboratories, Columbus, Ohio, for routine measurement of thermal expansion coefficients showed inelastic behavior even below the liquidus temperature of the electrolyte phase. Above the liquidus temperature, the samples collapsed under the force necessary for measurement.

This technique will not be pursued further, especially since some thermal expansion data are expected to be obtained during heating of tile samples in a static creep apparatus, which has been constructed. In this apparatus, shown schematically in Fig. 25, a tile sample is held under a controlled atmosphere between alumina plates, and is subjected to a variable load. Expansion and

Fig. 25.
Static Creep Apparatus

contraction of the sample are measured by a sensitive transducer located on the loading (upper) pedestal, which rests on the upper alumina plate. Thickness changes of 2 μ m are detectable, and pressures up to $\sim$ 700 kPa can be applied. Standard background curves are presently being obtained between 25 and 700°C.

C. Evaluation of Separator Materials

The housings of a single cell serve many of the same functions as intercell separators in cell stacks. They collect cell current and contain the reactive gases, forming a wet seal with the electrolyte at the cell edge. Type 316 stainless steel is used for housings at present, but an evaluation of other metals is desirable, especially for corrosion stability. The approach that is being taken is to form liners for the Type 316 stainless steel cell housings from thin sheets of the selected metals listed in Table 10, and to operate cells with these liners in place. Forming the liners is a drawing operation, and will yield some information about the possibility of shaping the alloys into intercell separators for stacks.

Table 10. Composition of Alloys for Housing Liners

Alloy	Composition, ^a wt %				$10^6 \times \alpha_T$ per °C ^b	Cost, ^c \$/lb
	C	Cr	Ni	Other		
<u>Austenitic Steel</u>						
347 ^d	0.08	17-19	9-13	(Nb + Ta), ~0.8	19.9	~1.50
310 ^d	0.25	24-26	19-22	---	17.5	1.85
316 ^d	0.03-0.08	~17	~12	Mo, ~2-3	19.9	1.42
<u>Ferritic Steel</u>						
430 ^d	0.12	14-18	---	---	13.1	0.80
405	0.08	11-14	---	Al, ~0.3	13.5	~0.75
446	0.20	23-27	---	---	13.7	1.42
<u>Other</u>						
IN 800 ^d	0.04	~33	~21	(Cu + Al + Ti), ~1.2	17.5	2.70
RA 333	0.05	~26	~42	Mo, ~3.8; W, ~2.7	16.9	5.10

^aBalance Fe.

^bFrom Ref. 27; for temperature range 0-1000°C.

^c0.5-in. regular plates for one ton quantity.

^dFoils received or on order.

The materials are mostly chosen from the various stainless steel alloys, which are not exceedingly expensive, and may well have adequate corrosion resistance. The alloys IN 800 and RA 333 have high chromium and nickel contents and are relatively expensive. Their thermal expansion coefficients are similar to those of austenitic stainless steels (300 series). These alloys are being included to aid in understanding the dependence of the high content of chromium and nickel in these alloys on wet-seal corrosion.

Initial experiments have been performed to line the cell housings. Foils (0.125 mm thick) of Types 321, 310 and 347 stainless steel were heated in a vacuum ($\sim 10^{-5}$ torr) at 1000°C for 0.5 hr and then quenched in argon to avoid the sensitization of steels in the temperature range from 500-850°C. A special die and plunger with rubber ring were machined for the desired shape of the liner. An appropriate size of foil was cut from the annealed stock and properly centered on the die, and the plunger with neoprene ring was then forced into the die by using a press. Once the liner was formed, it was inserted into the cell cavity by forcing the plunger into the cell. The liners prepared by this method were free of wrinkles, tears, and cracks. During the next quarter, the cells so prepared will be operated, and the corrosion behavior at the wet-seal areas will be investigated.

APPENDIX

ELECTROLYTE TILE CONDUCTIVITY

The IR or ohmic loss is one of the major contributions to the polarization in the molten carbonate fuel cell. As a result of the relatively low (compared to metals) conductivity of the melt, and to the presence of the nonconductive ceramic powder (LiAlO_2) used to contain the molten carbonate electrolyte, the electrolyte tile is a major source of ohmic resistance. The conductivity²⁸ of $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (1:1 mole ratio) at 600°C is $0.95 \Omega^{-1} \text{cm}^{-1}$, but the effective conductivity of the mixture of electrolyte and LiAlO_2 decreases by a factor which can be calculated from theoretical models.

The conductivity of electrolytes containing a dispersion of nonconducting, random particles was studied by Tobias and co-workers.²⁹⁻³¹ For spherical particles dispersed in a continuous electrolyte phase, the effective conductivity of the mixture, k_m , is related to the conductivity of the electrolyte, k_c , by the equation

$$\frac{k_m}{k_c} = \frac{8(2-f)(1-f)}{(4+f)(4-f)}$$

where f is the volume fraction of the particles. For oblate (flattened) spheroids (principal axes a, b, c) with $b/a = 3$ and $b = c$, the effective conductivity of the mixture is given by

$$\frac{k_m}{k_c} = \frac{(2-f)(1-f)}{(1+0.365f)(2-0.27f)}$$

When $b = c \gg a$, the oblate spheroid approaches the shape of the LiAlO_2 platelets observed with the scanning electron microscope. An equation of similar form for the effective conductivity of a mixture containing rod-like particles (where the diameter of the rod is assumed to be small relative to its length) can also be derived:

$$\frac{k_m}{k_c} = \frac{(2-f)(1-f)}{(1+0.335f)(2-0.33f)}$$

The shape of the nonconductive particles affects the effective conductivity of the mixture; however, the particle size has no effect, assuming that the particles are small relative to the volume of the mixture.

By means of the equations of Tobias and co-workers,²⁹⁻³¹ we can estimate the effective conductivity of electrolyte tiles. Using a density of 2 g/cm^3 for the molten carbonate electrolyte, 2.6 g/cm^3 for $\beta\text{-LiAlO}_2$, and 3.4 g/cm^3 for $\alpha\text{-LiAlO}_2$ we can calculate the dependence of the effective conductivity of the electrolyte tile on the amount of molten carbonate (Fig. 26). It can be seen that an electrolyte tile at 600°C containing 50 wt % $\text{LiCO}_3\text{-K}_2\text{CO}_3$ (1:1 mole ratio) and 50 wt % spherical LiAlO_2 particles would have an effective conductivity of $0.50 \Omega^{-1} \text{cm}^{-1}$ if the LiAlO_2 were $\alpha\text{-LiAlO}_2$ and $0.43 \Omega^{-1} \text{cm}^{-1}$ if it were $\beta\text{-LiAlO}_2$. This difference in effective conductivity arises from the difference in the densities of the α - and $\beta\text{-LiAlO}_2$, which affects the volume fraction, f , of the nonconducting phase.

Fig. 26. Relative Conductivity vs. Carbonate Content ($\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$, 1:1 mol ratio)

Since the conductivity of the molten carbonate is a function of temperature, the effective conductivity of electrolyte tile would also exhibit a dependence on temperature. As shown in Fig. 27, the effective conductivity of electrolyte tiles containing 50 wt % α -LiAlO₂ (spherical particles) and 50 wt % carbonate is a strong function of temperature, increasing by about 50% from 600 to 700°C. Furthermore, the effective conductivity of electrolyte tiles is dependent on the molar composition of the molten carbonate salts. The Li-rich eutectic (62 mol % Li_2CO_3 -38 mol % K_2CO_3) would yield an electrolyte tile with a higher effective conductivity than a tile containing the equimolar composition LiKCO_3 (0.71 vs. 0.61 $\Omega^{-1} \text{ cm}^{-1}$).

According to the equations of Tobias and co-workers,²⁹⁻³¹ the effective conductivity of an electrolyte containing a dispersion of nonconducting particles is a function of particle geometry. The effect of LiAlO₂ particle geometry on the effective conductivity of the electrolyte tile is shown in Fig. 28 for particles consisting of spheres, rods and oblate spheroids. For the calculation of the effective conductivity, it was assumed that the diameter of the rod is small relative to the length; for the case of the oblate spheroids, two models were considered $b/a = 6$, $b = c$ and $b/a = 3$, $b = c$. It is apparent that the effective conductivities of electrolyte tiles containing oblate spheroids are lower than those of electrolyte tiles containing rods or spheres. In particular, as the oblate spheroid approaches the shape of a LiAlO₂ particle with the platelet morphology, i.e., $b = c \gg a$, the effective conductivity becomes progressively lower.

Fig. 27. Relative Conductivity vs. Temperature.
Tile composed of spherical particles
of $\alpha\text{-LiAlO}_2$ (50 wt %)

The practical implications of this theoretical analysis for the molten carbonate fuel cell are:

(1) A higher effective conductivity and overall electrolyte tile density would be obtained from electrolyte tiles containing $\alpha\text{-LiAlO}_2$ than from those containing $\beta\text{-LiAlO}_2$ or $\gamma\text{-LiAlO}_2$, at the same weight percent LiAlO_2 . Therefore, the ohmic polarization of a molten carbonate fuel cell containing $\alpha\text{-LiAlO}_2$ in the electrolyte tile would increase if a phase change occurred in the LiAlO_2 during fuel cell life, provided that the amount of electrolyte in the tile did not change.

(2) Electrolyte tiles made from spherical or rodlike LiAlO_2 particles will have higher conductivities than those made from platelets of LiAlO_2 . Thus the conductivity of the tile can change if the morphology of the LiAlO_2 particles changes.

(3) The effective conductivity of LiAlO_2 /molten carbonate compositions used in electrolyte tiles is about 50% of the conductivity of the pure molten carbonates.

Fig. 28. Relative Conductivity vs. Particle Shape

(4) The LiAlO_2 particle size has no effect on the density or conductivity of the electrolyte tile (assuming that the LiAlO_2 particles are small relative to the dimensions of the electrolyte tile).

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