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ADVANCED FUEL CELL DEVELOPMENT

Progress Report for
July—September 1978

by

P. A. Finn, K. Kinoshita, G. H. Kucera,
R. D. Pierce, and J. W. Sim

U of C-AUA-USDOE

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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CHEMICAL ENGINEERING DIVISION
ADVANCED FUEL CELL DEVELOPMENT
July--September 1978

by

P. A. Finn, K. Kinoshita, G. H. Kucera,
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ABSTRACT

This report describes advanced fuel cell research and development activities at Argonne National Laboratory (ANL) during the period July-September 1978. These efforts have been directed toward understanding and improving the components of molten-carbonate-electrolyte fuel cells operated at temperatures near 925 K. The primary focus of this work has been the development of electrolyte structures that have good electrolyte retention and mechanical properties as well as long term stability, and on developing methods of synthesis amenable to mass production. The characterization of these structures and their stability is an integral part of this effort.

Synthesis studies have concentrated on the use of low-cost starting material to synthesize γ -LiAlO₂, the most stable allotrope of LiAlO₂ for the fuel cell conditions. Thermal stability and thermomechanical tests were performed on electrolyte mixtures to determine the effect of cell operating conditions on electrolyte tile longevity.

A square cell (10.6 cm) with an electrolyte tile containing γ -LiAlO₂ was tested. This tile was reinforced by a wire screen. Post-test examination of this cell after 1000 h of operation showed that the reinforced tile was considerably stronger than un-reinforced tiles. Future cells will utilize tiles with metal screen reinforcement.

SUMMARY

Electrolyte Development

The most stable allotrope of LiAlO₂ in the molten carbonate environment has been found to be γ -LiAlO₂. Consequently, synthesis procedures are being directed toward production of γ -LiAlO₂ from low-cost alumina. Studies during this period indicated that either a higher reaction temperature or a longer heating time is required to obtain γ -LiAlO₂ from physical mixtures containing low-cost aluminas instead of the more expensive γ -Al₂O₃ previously used.

Particle size analyses have been completed on several LiAlO_2 samples with surface areas of 5 to $80 \text{ m}^2/\text{g}$; there does not appear to be a correlation between particle-size distribution and the surface area of LiAlO_2 .

A major effort is under way to determine the thermal stability of LiAlO_2 under various conditions which may exist in operating cells. In these thermal tests, cold-pressed samples of $\gamma\text{-LiAlO}_2$ and alkali carbonates were heated in air for more than 1000 h at three temperatures--875, 925, and 975 K. The rate at which the sample surface area decreased was found to be rapid at 975 K, moderate at 925 K, and slow at 875 K. However, even at 875 K, the initial surface area was significantly reduced after 1000 h. In other tests, powder and cold-pressed mixtures of $\alpha\text{-LiAlO}_2$ and alkali carbonates were heated in air at 925 K for less than 100 h; the allotropic transformation of the α - to $\gamma\text{-LiAlO}_2$ and particle growth rate were much slower in the cold-pressed than the powder samples. This result is attributed to the slower escape of CO_2 (produced by the equilibrium reaction $\text{Li}_2\text{CO}_3 \rightleftharpoons \text{Li}_2\text{O} + \text{CO}_2$) from the electrolyte solution in the denser, cold-pressed pellets. Tiles, which are even more dense than the cold-pressed pellets, are expected to have even slower particle transformations.

Thermal expansion and creep (slumping) measurements were made on electrolyte mixtures containing either α -, β -, or $\gamma\text{-LiAlO}_2$. Test results for 11 pellets containing LiAlO_2 plus 55 wt % $\text{LiCO}_3\text{-K}_2\text{CO}_3$ at the eutectic melting temperature showed that the surface area, but not the particle shape, of the LiAlO_2 apparently affects the instantaneous creep and deformation in the pellet. Measurements of the instantaneous creep for applied stresses between 40 and 100 kPa indicated that, in general, the higher the surface area of the LiAlO_2 the less the effect of increasing stress. Studies to elucidate the effect of bimodal particle-size distributions on mechanical strength are under way.

Cell Testing

A square cell (SQ-5) employing a wire-screen-reinforced electrolyte tile containing $\gamma\text{-LiAlO}_2$ was operated for 1000 h, during which four thermal cycles (from 925 K to 575 K) were performed. Post-test examination showed that the structure of the tile was maintained and that cracks occurred only in the wet seal area, outside the reinforced area. Measurements to determine reactant gas cross-leakage indicated a slight increase over the operating time of the cell. Cell polarization was high, possibly due to poor anode wetting or to flooding of the cathode which was pre-wet with alkali carbonates prior to cell assembly.

I. INTRODUCTION

The advanced fuel cell studies at Argonne National Laboratory (ANL) are part of the DOE Second Generation Fuel Cell Program. The goal of this DOE program is the earliest possible introduction of high-efficiency generating systems based on molten-carbonate fuel cells, which have the capability of operating on coal or other fuels. At the present stage of development, the primary thrust of the program is directed to development of the fuel cell itself.

A molten carbonate fuel cell consists of a porous metal anode (presently nickel or an alloy of nickel), a porous nickel oxide cathode, an electrolyte structure which 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 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 "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 925 K. 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 to develop 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 the properties to tile behavior in cells is of major importance. Determination of the 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

The primary objective of the ANL effort on electrolyte development is to develop methods to synthesize LiAlO_2 that provide electrolyte structures with high strength and conductivity as well as good electrolyte retention. In addition, these synthesis methods must be amenable to the mass production of electrolyte structures. The relatively high cost of Degussa $\gamma\text{-Al}_2\text{O}_3$ (about \$6.70/kg), which is commonly used as the starting material to synthesize LiAlO_2 , has prompted development work at ANL to find an alternative, low-cost alumina.

A. Synthesis Methods

All evidence to date indicates that high-surface-area LiAlO_2 particles are essential in providing electrolyte tiles with good mechanical strength and electrolyte retention capabilities. Because $\gamma\text{-LiAlO}_2$ is the most stable allotrope of LiAlO_2 in the molten carbonate environment, efforts this quarter were directed toward the synthesis of high-surface-area $\gamma\text{-LiAlO}_2$. For the synthesis of LiAlO_2 , we used both $\gamma\text{-Al}_2\text{O}_3$ (Degussa, Type C) and the low-cost aluminas $[\text{Al}(\text{OH})_3$ and $\gamma\text{-AlOOH}]$ obtained from the Aluminum Company of America (ALCOA).

In the last report (ANL-78-71, p. 6), a procedure was described for the synthesis of $\gamma\text{-LiAlO}_2$ from Degussa $\gamma\text{-Al}_2\text{O}_3$. During this procedure, the allotropic transformation of α - to $\gamma\text{-LiAlO}_2$ was carried out at 1225 K for 16 h in air, thereby decreasing the LiAlO_2 surface area from 58 to 10 m^2/g . To obtain $\gamma\text{-LiAlO}_2$ with a higher surface area, we decided to lower the heat-treatment temperature of this step (see Fig. 1) to 1175 K. This modification in the synthesis procedure was found to result in only a slightly higher BET surface area (13 m^2/g) for the $\gamma\text{-LiAlO}_2$ sample. A scanning electron micrograph (SEM) of this example (Fig. 2) indicated that the small primary particles of $\gamma\text{-LiAlO}_2$ were fused together to form a larger agglomerate. After addition of $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (Step 3) and heat treatment at 875 K for 24 h in air/ CO_2 to prepare the electrolyte mixture, the surface area (14 m^2/g) and particle morphology of the sample material remained essentially unchanged. The $\gamma\text{-LiAlO}_2$ prepared by the method outlined in Fig. 1 has a slightly lower BET surface area than that previously obtained (ANL-78-40, p. 6) by the two-stage heat treatment (775 K for 24 h followed by 975 K for 16 h) of a physical mixture of $\gamma\text{-Al}_2\text{O}_3/\text{LiOH-Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (14 vs. 17 m^2/g). The particle morphology of the $\gamma\text{-LiAlO}_2$ obtained by the two methods of synthesis also differs, more sintering was found in particles produced by the procedure depicted in Fig. 1. Evaluation of electrolyte mixtures containing $\gamma\text{-LiAlO}_2$ produced by both methods will be made in cell tests and thermomechanical tests.

Experiments also were conducted to prepare $\gamma\text{-LiAlO}_2$ from low-cost alumina by heat treatment of physical mixtures of the following: (1) Li_2CO_3 , K_2CO_3 and $\text{Al}(\text{OH})_3$ or $\gamma\text{-AlOOH}$ and (2) LiOH , Li_2CO_3 , K_2CO_3 , and $\text{Al}(\text{OH})_3$.

Previous results (ANL-77-29, p. 7) showed that physical mixtures of Li_2CO_3 , K_2CO_3 , and $\gamma\text{-LiAlO}_2$ (Degussa) heated at 875 K for 24 h produced $\alpha\text{-LiAlO}_2$ with high surface areas (70-80 m^2/g); however, prolonged heating (90 h) resulted in the formation of a minor phase of $\gamma\text{-LiAlO}_2$ in addition to a major phase of $\alpha\text{-LiAlO}_2$. Two alumina/ $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ samples, one containing

Fig. 1. Preparation of Electrolyte Mixture Containing a Major Phase of γ -LiAlO₂

Fig. 2. Scanning Electron Micrograph of γ -LiAlO₂ Obtained from α -LiAlO₂ Heated at 1175 K for 16 h (Sample 134-5)

$\text{Al}(\text{OH})_3$ and the other $\gamma\text{-AlOOH}$, were heated at 875 K for 47 h; this heat treatment resulted in particles of $\alpha\text{-LiAlO}_2$ with low surface areas--22 m^2/g for the $\text{Al}(\text{OH})_3$ sample and 11 m^2/g for the $\gamma\text{-AlOOH}$ sample. Owing to their low surface area, these two samples are not considered useful for cell testing purposes. However, they will be examined to determine the thermomechanical behavior of pellets containing low-surface-area $\alpha\text{-LiAlO}_2$. Since $\gamma\text{-LiAlO}_2$ was not produced by heating the physical mixtures [Li_2CO_3 , K_2CO_3 , and $\text{Al}(\text{OH})_3$] at 875 K, another sample was heated at a higher temperature (975 K) for 24 h. X-ray analysis indicated that a major phase of $\alpha\text{-LiAlO}_2$ and a very minor phase of $\gamma\text{-LiAlO}_2$ were formed. Apparently, a higher temperature or a longer heating time at 975 K is required to form pure $\gamma\text{-LiAlO}_2$ from a physical mixture of alkali carbonates and $\text{Al}(\text{OH})_3$. In view of the lack of success in producing $\gamma\text{-LiAlO}_2$ from the above physical mixture, further examination of this synthesis method was discontinued.

The low-temperature synthesis (775 K for 1.5 to 22 h) of $\gamma\text{-LiAlO}_2$ from physical mixtures of $\gamma\text{-Al}_2\text{O}_3$ (Degussa)/ $\text{LiOH-Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ was described in previous quarterly reports (ANL-78-16, p. 7; ANL-78-40, p. 12). The preparation of $\gamma\text{-LiAlO}_2$ by the same procedure from starting materials containing low-cost

Fig. 3. Synthesis of LiAlO_2 from Physical Mixtures of $\text{Al}(\text{OH})_3/\text{LiOH-Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$

aluminas was not successful, β -LiAlO₂ and γ -Al₂O₃ being the major products obtained. Therefore, we re-examined the synthesis method for the preparation of γ -LiAlO₂ from a physical mixture of Al(OH)₃, LiOH, Li₂CO₃, and K₂CO₃; two different synthesis methods, outlined in Fig. 3, were developed. In method I, only one-half the amount of Li₂CO₃-K₂CO₃ required to make an electrolyte mixture containing 55 wt % alkali carbonate was physically mixed with LiOH and Al(OH)₃. After heat treatment of the physical mixture at 775 K for 30 h, the other half of the Li₂CO₃-K₂CO₃ was added. In method II, 55 wt % Li₂CO₃-K₂CO₃ was physically mixed with LiOH and Al(OH)₃ prior to the first heat treatment. For samples prepared by both methods, β -LiAlO₂ was the major product after the first heat treatment and approximately equal amounts of α -, β -, and γ -LiAlO₂ were produced after the second heat treatment. The surface areas of the LiAlO₂ samples were 15 m²/g for method I and 20 m²/g for method II. A scanning electron micrograph of the LiAlO₂ sample produced by method II is shown in Fig. 4; submicrometer-sized particles of LiAlO₂ clumped together into larger agglomerates were evident in samples prepared by both methods.

Fig. 4. Scanning Electron Micrograph of LiAlO₂ (approximately equal amounts of α -, β -, and γ -LiAlO₂) Obtained from LiOH/Al(OH)₃/Li₂CO₃-K₂CO₃ Heated at 775 K for 4 h and 975 K for 2 h (Sample 134-20).

The fact that a substantial amount of α -LiAlO₂ is obtained by the synthesis methods outlined in Fig. 3 indicates that alternative experimental conditions must be considered to prepare γ -LiAlO₂ from low-cost aluminas. The alumina particle size and the rate of reaction to form LiAlO₂ both appear to affect the allotrope of LiAlO₂ obtained by heating physical mixtures of alumina, LiOH, Li₂CO₃, and K₂CO₃ at 775 K. In the future, heat-treatment temperatures >775 K will be used to increase the rate of reaction to form LiAlO₂ from these physical mixtures.

B. Particle Size Analysis

In the molten carbonate fuel cell, the electrolyte retention capability and the thermomechanical behavior of electrolyte tiles are dependent on the surface area as well as particle size and particle size distribution of the LiAlO₂. Particle size measurements were made on a variety of LiAlO₂ samples prepared by the methods outlined in Table 1. These measurements were performed by Particle Data Laboratory (Elmhurst, Illinois) using the computerized ELZONE™ system. The experimental technique was described previously (ANL-78-40), p. 4). The allotrope, particle shape and surface area of the samples are also included in the table. Scanning electron micrographs of several of the LiAlO₂ samples listed in Table 1 were presented in a previous quarterly report (ANL-78-40, pp. 8, 10, and 16).

Figure 5 shows the volume distribution curves (*i.e.*, relative frequency by volume of LiAlO₂ vs. equivalent particle diameter) for samples 98-127 (α -LiAlO₂) and 98-96 (γ -LiAlO₂). Sample 98-127 was obtained by a synthesis method used to prepare the high-surface-area α -LiAlO₂ tested in cells SQ 1-4 (ANL-78-40, p. 29 and ANL-78-71, pp. 19-20). Sample 98-96 was obtained by a method similar to that used to prepare the γ -LiAlO₂ contained in the electrolyte tile tested in cell SQ-5 (reported in Section III). Both samples exhibited a bimodal-type particle-size distribution. A mode occurs at ≤ 1 μ m for both samples, while a second mode is present at about 10 μ m for sample 98-127 and about 7 μ m for sample 98-96.

Figure 6 shows the volume distribution curves for two samples of β -LiAlO₂ with rod-shaped particles. As shown in Table 1, sample 98-114 was prepared from low-cost Al(OH₃) and had a surface area of 13 m²/g. Sample 56-141A was prepared from Degussa γ -Al₂O₃ and had a surface area of 7 m²/g. As can be seen in the figure, sample 98-114 has a narrow particle size distribution, with a mode at about 1.4 μ m. On the other hand, sample 56-141A exhibited a broad particle-size distribution. SEM examination of sample 56-141A indicated that some of the rod-shaped particles may be fused together; this could also account for the presence of the relatively large particles.

The volume distribution curves for two other samples of β -LiAlO₂ are plotted in Fig. 7. The surface areas for these two samples are as follows: 98-123, 11 m²/g, and 18-6A, 60 m²/g; both contained clump-shaped particles. Sample 18-6A has a distribution curve with a mode at about 9 μ m; these particles of β -LiAlO₂ must contain micropores to account for the high surface area

Table 1. Description of LiAlO_2 Samples Used for Particle Size Analysis

Sample No.	Reactant Mixture	Alumina	Heat-Treatment Conditions			LiAlO ₂ Physical Properties		
			Temp., K	Time, h	Gas Environment	Allotrope	Particle Shape	Surface Area, m ² /g
98-127	$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3^{\text{a}}$	Degussa	875	24	CO_2/air	$\alpha\text{-LiAlO}_2$	clumps	78
98-96	$\text{LiOH-Li}_2\text{CO}_3\text{-K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3^{\text{a}}$	Degussa	775	2	air	$\gamma\text{-LiAlO}_2$	clumps	17
			975	16	CO_2/air			
56-141A	$\text{LiOH-KOH}/\gamma\text{-Al}_2\text{O}_3^{\text{b}}$	Degussa	300	1	CO_2/air	$\beta\text{-LiAlO}_2$	rods	7
			725	7.5	CO_2/air			
98-114	$\text{LiOH-KOH}/\text{Al}(\text{OH})_3^{\text{b}}$	ALCOA	300	1.5	CO_2/air	$\beta\text{-LiAlO}_2$	rods	13
			775	1	CO_2/air			
98-123	$\text{LiOH}/\gamma\text{-Al}_2\text{O}_3^{\text{a}}$	Degussa	775	1.5	air	$\beta\text{-LiAlO}_2$	clumps	11
18-6A	$\text{LiOH-KOH}/\text{Al}(\text{OH})_3^{\text{c}}$	ALCOA	LiAlO ₂ precipitated from methanol solution, then heated at 725 K for 1.5 h in air.			$\beta\text{-LiAlO}_2$	clumps	60

^aPhysical mixture.^bImpregnated.^cThe $\text{Al}(\text{OH})_3$ was completely dissolved in solution.

Fig. 5. Volume Distribution Curves for α - and γ - LiAlO_2

Fig. 6. Volume Distribution Curves for Rod-Shaped Particles of β - LiAlO_2 .

(60 m²/g). The scanning electron micrograph of this sample (ANL-78-14, p. 16) shows that the particles consist of a tightly packed network of small lamina, which are probably fused together into a porous structure. The data in Fig. 7 also show that a substantial amount of large particles is present in sample 98-123. This result was confirmed by SEM, which showed that the β -LiAlO₂ was present in the sample as large clumps.

Fig. 7. Volume Distribution Curves for Clump-Shaped Particles of β -LiAlO₂

C. Thermal Stability Tests

Tests are presently in progress to determine the effects of temperature, treatment time, gas environment, and electrolyte composition on the thermal stability of LiAlO₂. The changes observed in the allotropic form, size, shape, and surface area of the LiAlO₂ particles are used to assess the relative stability of the various LiAlO₂ forms under different operating modes. Using these observations, we are able to estimate the effect of different fuel cell operating conditions on both the longevity and the electrochemical behavior of the electrolyte tile.

During this quarter, two series of thermal tests were initiated. In the first, a detailed assessment was conducted on the thermal stability in air of γ -LiAlO₂, which has been shown to be the most stable of the three LiAlO₂ allotropes. (Air was chosen as the environment for heat treatment because it has been shown to have the most detrimental effects of the allotropic stability.) In the second series, the thermal stability of α -, β -, and γ -LiAlO₂ at 925 K, the anticipated operating temperature of the molten carbonate fuel cell, was investigated. In our previous thermal tests, powder samples were used. To ensure that all samples were similar, the present tests were conducted with cold-pressed pellets (about 1.3-cm dia, by about 0.8-cm high) consisting of 45 wt % LiAlO₂ and 55 wt % carbonate (62 mol % Li₂CO₃-38 mol % K₂CO₃). The α -LiAlO₂ samples were about 70% $\pm$ 5 theoretical density, the β - and γ -LiAlO₂ samples were about 80% $\pm$ 5. In these tests, pellets of the same starting material were heated for times ranging from 6 h to over 1000 h. X-ray diffraction analysis, scanning electron microscopy (SEM), and BET surface areas were used to characterize the samples both before and after the thermal tests.

Table 2 shows the changes that occurred during the heat treatment at 975 K in air of γ -LiAlO₂ with two different surface areas--16.9 and 7.6 m²/g. Sample 108-145, shown in Fig. 8, consisted of clumps of small LiAlO₂ particles with a surface area of 16.9 m²/g. Heat treatment of this starting material for only 6 h produced a dramatic decrease in the surface area, from 16.9 to 10.2 m²/g; SEM of this material showed bipyramids which ranged in size from

Table 2. Changes Produced in γ -LiAlO₂ Pellets after Heating at 975 K in Air

Sample No.	Time, h	Surface Area ^a m ² /g	Particle Size, μ m	Particle Shape ^b
108-145 ^c	--	16.9	<0.5	clumps, small particles
108-159	6	10.2	0.25-4	clumps, small particles and bipyramids
108-152	20	3.2	0.5-4	bipyramids
108-155	256	0.85	0.5-8	
108-172	1000	0.55	1-10	
108-220	2400	0.5	2-10	
108-153 ^c	--	7.6	1 by 0.25	rods
108-162	20	5.2	1 by 0.5	rods
108-176	240	2.2	1 by 0.5 and 1-10	rods and bipyramids
108-221	1000	0.2	1-10	bipyramids

^aThe surface areas reported are $\pm$ 20% for $\geq$ 5 m²/g and $\pm$ 50% for $<$ 2 m²/g.

^bDetermined by scanning electron microscopy.

^cStarting material.

Fig. 8. Scanning Electron Micrograph of γ -LiAlO₂ (16.9 m²/g) prior to Heat Treatment (sample 108-145).

Fig. 9. Scanning Electron Micrograph of γ -LiAlO₂ (0.55 m²/g) after 1000 h at 975 K in Air (sample 108-172).

0.25 to 4 μm . As the heating time was increased, sintering of the material continued, the surface area being reduced to 0.55 m^2/g after 1000 h. After 1000 h SEM (Fig. 9) showed the shape of the LiAlO_2 to be large bipyramids (1 to 10 μm). The dramatic difference in appearance between Fig. 9 and Fig. 8 indicates that tiles composed of these two materials will have quite different properties (see Section II.D).

Sample 108-153 (Fig. 10) consisted of small LiAlO_2 rods with a surface area of 7.6 m^2/g . As can be seen in Table 2, heating pellets of this starting material at 975 K in air resulted in a steady decrease in surface area as the heating time was increased. Although the rate of change was not as rapid as that observed in sample 108-145, the resulting material after 1000 h at 975 K is essentially identical to that shown in Fig. 9. Therefore, the particles of $\gamma\text{-LiAlO}_2$ preferentially transform to large bipyramids at 975 K in air.

Fig. 10. Scanning Electron Micrograph of $\gamma\text{-LiAlO}_2$ (7.6 m^2/g) prior to Heat Treatment (sample 108-153).

Table 3 shows the effect of heating sample 108-145 ($\gamma\text{-LiAlO}_2$, 16.9 m^2/g) for up to 1000 h at a lower temperature than previously, 925 K. As can be seen in the table, significant particle growth was produced after 20 h. The growth rate is slower than that discovered when this type of pellet was heat treated at 975 K; but, after 1000 h, the bipyramids formed are similar in size to those shown in Fig. 9 and the surface area is 1.4 m^2/g . At 925 K, therefore, the $\gamma\text{-LiAlO}_2$ in contact with air can be expected to grow in size and decrease in surface area to a considerable extent.

Table 3. Changes Produced in γ -LiAlO₂ Pellets after Heating at 925 K in Air

Sample No.	Time, h	Surface Area, ^a m ² /g	Particle Size, μ m	Particle Shape
108-145	--	16.9	<0.5	clumps, small particles
108-166	6	17.1	<0.5	
108-167	20	14.8	0.25-1	clumps, small particles, and bipyramids
108-173	240	1.1	0.5-6	bipyramids
108-177	1000	1.4	0.5-10	bipyramids

^aThe surface areas reported are $\pm 10\%$ for ≥ 5 m²/g and $\pm 50\%$ for < 2 m²/g.

Table 4 shows the effects of heating sample 108-145 for up to 1000 h in air at an even lower temperature, 875 K. After 1000 h at 875 K, the starting material showed no change in morphology (see Fig. 11) or particle size, and only a slight decrease in surface area (from 16.9 to 13.8 m²/g). Thus, the growth characteristics of sample 108-145 are much different when the material is heat treated at 875 K than when it is held at 925 or 975 K in air. The results after 2400 h of heating are not yet available.

Table 4. Changes Produced in γ -LiAlO₂ Pellets after Heating at 875 K in Air

Sample No.	Time, h	Surface Area, ^a m ² /g	Particle Size, μ m	Particle Shape
108-145	--	16.9	<0.5	clumps, small particles
108-170	6	17.7	<0.5	
108-171	20	b	<0.5	
108-165	240	b	<0.5	
108-174	1000	13.8	<0.5	

^aThe surface areas reported are $\pm 10\%$ for ≥ 5 m²/g and $\pm 50\%$ for < 2 m²/g.

^bData not available.

Figure 12 shows the surface area of the γ -LiAlO₂ pressed samples as a function of time of heat treatment for the three temperatures studied--875, 925, and 975 K. Final conclusions cannot yet be made, but the instability of the morphology of γ -LiAlO₂ during long-term operation of molten carbonate fuel cells may prove troublesome even at 925 K if the tiles are exposed to air.

Fig. 11. Scanning Electron Micrograph of γ -LiAlO₂ (13.8 m²/g) after 1000 h at 875 K in Air (sample 108-174).

In the second series of tests, LiAlO₂ (α , β , and γ) pellets were heated at 925 K for 3 to 2400 h in one of the following three environments: air, CO₂, and 80% H₂-20% CO₂ saturated with H₂O at room temperature. These tests were conducted to determine the effect of initial surface area on the rate of allotropic transformation, surface area reduction, and particle growth.

Table 5 shows the transformations of α -LiAlO₂ pellets heated at 925 K in air for 3 to 318 h. In the first case, the pressed starting material (sample 108-168) contained large porous clumps (Fig. 13) of α -LiAlO₂ with a surface area of 75.4 m²/g. A powder sample of the same material as 108-168 was heated in air at 925 K for about 22 h; the results of this heat treatment are also presented in Table 5. X-rays and SEM of the powder sample after heat treatment were similar to those reported previously for powders of high-surface-area α -LiAlO₂ heated at 925 K for about 24 h in air (ANL-78-71, p. 11). They showed small bipyramids clustered together in clumps (see Fig. 14), primarily γ -LiAlO₂. In contrast, the material produced from the cold-pressed pellet after the same heat treatment (108-188 in Table 5) had essentially the same particle shape as the starting material and primarily consisted of α -LiAlO₂. After 318 h, the particle shape of the pressed material (sample 108-222) resembled that of the powder sample after 22 h of heat treatment (compare Figs. 14 and 15); α -LiAlO₂ was still the major allotrope, although a slight increase was found in the amount of γ -LiAlO₂. In addition, the surface area after 318 h of heat treatment had been reduced from 75.4 to 5 m²/g. Thus, high-surface-area α -LiAlO₂ will be converted quickly to low-surface-area α -LiAlO₂ in air at 925 K.

Fig. 12. Surface Area Reduction of γ -LiAlO₂ Pellets as a Function of Time.

The difference in behavior between a powder and a cold-pressed pellet in an air environment can be attributed to the differences in the bulk surface area-to-volume ratio of the two materials. For both samples, some of the Li₂CO₃ present dissociates into Li₂O and CO₂. However, for the powder, the CO₂ is rapidly dispersed, and an excess of oxide and hydroxide ions remain which promote faster allotropic transformation and recrystallization because of increased solubility of the LiAlO₂ in the liquid phase. The CO₂ is also dispersed from a cold-pressed pellet, but at a rate about 10 times slower. For a hot-pressed pellet in which the density is >95% of theoretical, the rate of CO₂ loss is expected to be slowed down to an even greater extent. This effect would result in slower sintering and slower allotropic transformations.

As also shown in Table 5, sample 108-175 contained dense chunks of LiAlO₂ (Fig. 16) with a much lower surface area than that of sample 108-168 (25.9 vs. 75.4 m²/g). X-ray examination of this material after 318 h at 925 K (sample 108-219) indicated that no transformation to γ -LiAlO₂ had occurred. Figure 17 is an SEM after 318 h of heat treatment. Some sintering can be detected; however, the extent cannot be assessed until the surface area measurements are available. Sintering of the α -LiAlO₂ appears to be partially inhibited by the low starting surface area. From the data in Table 5, we concluded that the transformation of α - to γ -LiAlO₂ is inhibited when low-surface-area material is used.

Table 5. Changes Produced in α -LiAlO₂ Pellets (powder and cold-pressed) after Heat Treatment at 925 K in Air

Sample No.	Time, h	LiAlO ₂ Phase	Surface Area, ^a m ² /g	Particle Shape
108-168 ^b	--	α	75.4	large porous clumps bipyramids (<0.25 to 2 μ m)
108-182	3	α	^c	
108-188	22	α , γ^d	50	
108-222	318	α , γ^e	5.0	
108-238 (powder sample)	22	γ , α^e	b	
108-175 ^b	--	α	25.9	irregular shaped particles denser particles
108-185	3	α	^c	
108-193	22	α	10	
108-219	318	α	4	

^aThe surface areas reported are $\pm 10\%$ for ≥ 5 m²/g and $\pm 50\%$ for < 2 m²/g.

^bStarting material.

^cData not available.

^dVery minor.

^eMinor.

Fig. 13. Scanning Electron Micrograph of α -LiAlO₂ (75.4 m²/g) prior to Heat Treatment (sample 108-168).

Fig. 14. Scanning Electron Micrograph of α -LiAlO₂ after 22 h at 925 K in Air (sample 108-238).

Fig. 15. Scanning Electron Micrograph of α -LiAlO₂ (5.0 m²/g) after 318 h at 925 K in Air (sample 108-222).

Fig. 16. Scanning Electron Micrograph of α -LiAlO₂ (25.9 m²/g) prior to Heat Treatment (sample 208-175).

Fig. 17. Scanning Electron Micrograph of α -LiAlO₂ after 318 h at 925 K in Air (sample 108-219).

Table 6. Changes Produced in α -LiAlO₂ Pellets after Heating at 925 K in H₂-CO₂-H₂O^a

Sample No.	Time, h	LiAlO ₂ Phase	Surface Area, ^b m ² /g	Particle Shape
108-168 ^c	--	α	75.4	large porous clumps
108-194	3	α	d	d
108-212	22	α	50	large porous clumps
108-232	314	α , γ (minor)	3.5	bipyramids (<0.25 - $3 \mu\text{m}$)
108-175 ^c	--	α	25.9	irregular shaped
108-197	3	α	d	d
108-215	22	α	6	denser
108-235	314	α	4	denser

^aThis environment contains 80% H₂ and 20% CO₂ saturated with H₂O (at 298 K).

^bThe surface areas reported are $\pm 10\%$ for $\geq 5 \text{ m}^2/\text{g}$ and $\pm 50\%$ for $< 2 \text{ m}^2/\text{g}$.

^cStarting material.

^dData not available.

The same starting materials as listed for samples 108-168 and 108-175 in Table 5 were heated at 925 K for 3 to 314 h in 80% H₂-20% CO₂ that had been saturated with water at room temperature. Results of X-ray and SEM analyses, given in Table 6, were similar to those given in Table 5.

Previous tests with powder samples in an H₂-CO₂-H₂O environment also produced results similar to those given in Table 6 (ANL-78-71, pp. 9-13). For both the powder and cold-pressed samples, the CO₂ present in the H₂-CO₂-H₂O environment retards the recrystallization and the allotropic transformation of α -LiAlO₂. However, as can be inferred from Table 6, significant area reduction occurs in only 314 h with a pressed pellet; therefore, the surface area of α -LiAlO₂ is expected to be reduced during the operation of a fuel cell. Insufficient data have been collected to determine whether the rate of sintering is affected by the initial surface area.

The following conclusions can be made from the thermal test results to date. First, the primary problem with the LiAlO₂ matrix is loss of surface area. However, for heat treatment of γ -LiAlO₂ in air, the surface area loss does not appear to be affected by sample surface area, but is affected strongly by temperature. Second for heat treatment of α -LiAlO₂, the rate of surface area loss may be affected by the original sample's surface area (additional tests are needed to verify this); and the allotropic transformation to γ -LiAlO₂ is inhibited for samples with low initial surface area. Third, the use of a CO₂ environment for heat treatment appears to retard both surface area loss and allotropic transformation; this result appears to be due to a reduction in the LiAlO₂ solubility. The third conclusion will be studied further in order to optimize cell performance.

D. Thermomechanical Tests

Thermal expansion and creep measurements were made on several electrolyte mixtures. Eleven small pellets (13-mm dia) containing LiAlO_2 and 55 wt % $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (62 mol % Li_2CO_3 -38 mol % K_2CO_3) were hot-pressed and tested in the high-sensitivity thermomechanical apparatus described previously (ANL-78-71, p. 7). The thermomechanical behavior of each pellet was monitored during two to four thermal cycles while under a compression stress of either 41 or 103 kPa. During a typical thermal cycle (duration, 10 h), the pellet is heated at a rate of about $15^\circ\text{C}/\text{min}$ to about the melting temperature of the $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic (764 K), maintained at that temperature for approximately one half hour, heated at the cell operating temperature (925 K) for about 2 h, and finally cooled to room temperature at a rate of $3^\circ\text{C}/\text{min}$. In order to correlate the thermal behavior of the pellets with the measurable physical properties (particle shape, size, and size distribution) of the LiAlO_2 matrix, the LiAlO_2 powders were characterized by X-ray diffraction analysis, SEM, and BET surface area and particle size measurements. Hot-pressing conditions were kept nearly constant to eliminate the effect of the variation in green (as-pressed) density of the pellet on its thermal behavior.

Figure 18 shows the thickness change of pellet 98-115 ($\gamma\text{-LiAlO}_2$ and 55 wt % $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$) during a single thermal cycle while under a stress of 41 kPa; this pellet exhibits what is considered to be desirable thermal behavior. The overall characteristics seen in this thermal cycle are generally typical of those matrix materials that exhibit good mechanical strength.

Fig. 18. Thermal Response of $\gamma\text{-LiAlO}_2$ Under a Stress of 41 kPa

Table 7 is a summary of the instantaneous creep values (sudden thickness change at eutectic melting temperature) for each pellet tested to date. The data, which have been arranged according to increasing surface area for each allotropic form of LiAlO_2 , show an apparent correlation between surface area and mechanical strength i.e., instantaneous creep decreases as surface area

Table 7. Instantaneous Creep Values of Pellets Containing LiAlO₂

Pellet No.	LiAlO ₂ Allotrope	Particle Shape	Pellet Thickness, mm	Surface area, m ² /g (±10%)	Green Density, g/cm ³	Stress, kPa	Instantaneous Creep, % Compression ^a
134-3	α	large clumps	4.2	11	2.55	41	>50
98-18	50% α-50% β	clumps & rods	3.6	44	2.43	41	7
98-127 ^b	α	clumps	4.1	78	2.51	41	<1
						103	3
98-132	β	rods & clumps	4.3	8	2.32	41	40
98-114 ^c	β	rods	6.3	13	2.36	103	>50
98-137 ^b	β	clumps	3.5	20	2.34	41	1
						103	4
98-147	γ	large and small clumps	3.2	10	2.31	41	13
98-96	γ	bipyramids	2.2	17	~2.3	41	-2 ^d
98-115	γ	clumps	5.4	26	2.30	41	1
18-13	50% γ-50% α	sporge-like	4.0	52	2.43	41	0

^aPercent of original thickness.^bPellet was tested for two thermal cycles under each load.^cReported previously in ANL 78-71, p. 17.^dPellet showed slight expansion.

increases for any given allotropic form. Comparing pellets 134-3 (α -LiAlO₂, clumps), 98-132 (β -LiAlO₂, rods and clumps) and 98-147 (γ -LiAlO₂, large and small clumps), all of which have approximately the same surface area, we were unable to find a correspondence between mechanical strength and particle shape.

In order to evaluate the effect of stress on the mechanical strength of a pellet, duplicate pellets of several mixtures were hot-pressed and tested. These data, presented in Table 8, show that, in general, the higher the surface area of the LiAlO₂ the less effect increasing stress has on the mechanical strength. The anomalous behavior of pellet No. 98-18 (44 m²/g) may be due to the fact that this electrolyte mixture contains LiAlO₂ particles of two different shapes--high-surface-area α -LiAlO₂ (clump-shaped) and low-surface-area β -LiAlO₂ (rod-shaped particles). Studies to elucidate the effect of bimodal particle-size distributions on mechanical strength of the electrolyte tile are currently under way (see Section II.B).

Table 8. Effect of Stress on Instantaneous Creep Values of Pellets.

Sample No.	LiAlO ₂ Allotrope	Particle Shape	Surface area, m ² /g ($\pm 10\%$)	Stress, kPa	Instantaneous Creep, ^a % Compression
98-132	β	rods & clumps	8	41 103	40 ≥50
98-96 } 92-101A }	γ	bipyramids	17	41 86	-2 7 ^c
98-115	γ	clumps	26	41 103	>1 -2
98-18	50% α -50% β	rods & clumps	44	41 86	7 29 ^c
18-13	50% γ -50% α	sponge-like	52	41 103	0 <1

^aPercent of original thickness.

^bSamples 98-96 and 92-101A were made from the same starting material at different times.

^cInstantaneous creep value reported previously in ANL-78-40, p. 28 for a stress of 86 kPa.

III. CELL TESTING

During this quarter, Cell SQ-5 was constructed with an electrolyte tile that was reinforced with a metal screen employed by the Institute of Gas Technology (IGT) in their tiles. The LiAlO_2 particles used in the tile were primarily $\gamma\text{-LiAlO}_2$ with a surface area of $25.7 \text{ m}^2/\text{g}$, and the thickness of the tile was 0.20 to 0.22 cm. As mentioned earlier the γ phase of LiAlO_2 is desirable because it is more stable than either α - or $\beta\text{-LiAlO}_2$ with respect to phase transformation. The electrode protrusions were 0.002 to 0.008 cm for the anode* and -0.008 cm to -0.013 cm for the cathode.†

The purpose of the screen was to strengthen the tile and prevent cracking during thermal cycling (up to the melting point of the alkali carbonates). The reinforcing screen was woven from Kanthal‡ Type A-1 wire (0.013-cm dia), with 20 wires per 2.54 cm. This type of wire, which contains 5.5% Al, 22% Cr, 0.5% Co and a balance of Fe, form a tightly adherent aluminum-oxide coating when heated in air. The aluminum-oxide coating helps prevent corrosion of the wire by the molten carbonates in the electrolyte tile. The reinforcing screen used in Cell SQ-5 had been heat treated at 925 K for 24 h in air before use in the electrolyte tile. (In subsequent tiles, the reinforcing screen was heat treated at 925 K for 72 h. The prolonged heat treatment produces a flatter, less flexible screen, which facilitates centering of the screen in the tile during pressing. The imprint of the reinforcing screen was visible on the surface of the tile used in Cell SQ-5; in subsequent tiles, the screen has not been visible at the surface of the finished tile.)

Space was left in the cathode compartment for expansion of the electrode upon oxidation from nickel to NiO . Expansion of the cathode in previous cells apparently caused compression of the anode (see ANL 78-71, p. 20). When porous nickel samples were oxidized in air at 650°C (outside of the cell), expansion (about 20%) was observed only when the sample had been wetted by a carbonate film. Thus to ensure contact of the cathode with the tile, the electrode was prewetted with alkali hydroxides, which were converted to alkali carbonates before use in the cell.

Cell SQ-5 was operated for 1000 h during which time it was subjected to four thermal cycles. The heating and cooling rate during the thermal cycles was about $3^\circ\text{C}/\text{min}$. During cell operation, the wet-seal efficiency** was from 94 to 100% for both electrodes; but the cell resistance was from 18 to 20 $\text{m}\Omega$, which is high and may indicate poor anode wetting. Cell voltage (IR included) at various current densities are shown as a function of operating time in Fig. 19. The cell voltage is low, possibly because the anode was poorly wetted or the pre-wetted cathode was flooded with alkali carbonates. Reactant

* Union Carbide No. 306-28-18-1, 10.2- μm mean pore size, 77% porosity.

† Union Carbide No. 306-28-18-1, pre-wetted with alkali carbonates (0.37 g).

‡ The Kanthal Corp., Bethel, Conn.

** Flow rate out divided by flow rate in (at 102.7 cc/min for anode, 203.7 cc/min for cathode).

Fig. 19. Cell Performance vs. Operating Time for Cell SQ-5

gas cross-leakage was also monitored throughout operation (see Appendix for a description of the analytical method), and these results are shown in Fig. 20. Cross-leakage occurred early in cell operation, which may indicate that a crack developed in the tile during the initial heating of the cell.

Fig. 20. Cross-leakage in Cell SQ-5

Immediately following each thermal cycle the cross-leakage increased, but with continued operation at 925 K (i.e., between the thermal cycles) the cross-leakage decreased. This result suggests two possibilities: additional cracks may form during the thermal cycles, or any existing cracks may become enlarged. After several hours at cell operating temperature, however, the crack(s) apparently decrease in size. Nonetheless, the cross-leakage is larger at the end of cell operation than at the beginning, indicating an overall increase in cross-leakage.

Post-test examination of the cell showed that the reinforced electrolyte tile was considerably stronger than un-reinforced tiles. For the first time at ANL, the tile was removed from the cell completely intact after operation. In previous cell tests of shorter duration, with fewer thermal cycles, the tile could not be removed in one piece. Several small (about 0.1 to about 1 mm) cracks were observed in the wet-seal area of the tile, but none was apparent in the area between the electrodes. No reinforcing screen was present in the area where the cracks were observed. This suggests that, if the reinforcing screen extended to the edge of the electrolyte tile, the cracks might not have developed. The tile separated easily from the anode, indicating that poor wetting of the anode may have occurred.

Because reinforcement of the tile greatly improves its mechanical strength, future cells will utilize tiles with metal screen reinforcement. In recently pressed tiles, the Kanthal screen extends to within about 1 mm of the perimeter of the tile. This measure should eliminate tile cracking in the wet-seal area, and it may improve wet-seal efficiency and reduce reactant gas cross-leakage.

APPENDIX

Analytical Method for Determining Reactant Gas Cross-Leakage

An important function of the electrolyte tile is to separate the reactant gases (fuel and oxidant). In cells tested at ANL, the fuel consists of 80% H₂, 20% CO₂ plus H₂O at a dew point of 298 K, while the oxidant contains 14.5% O₂, 28% CO₂ and 57.5% N₂. Since the fuel contains no N₂, analyzing the anode exhaust for the presence of N₂ will indicate (1) cross-leakage of oxidant into the anode compartment through the tile, or (2) leakage of air into the anode compartment past the wet-seal. Application of a differential pressure to the tile (cathode pressure higher than anode pressure) should increase cross-leakage of oxidant over and above that measured with no differential pressure. This procedure can help to distinguish between the two possible sources of N₂ in the anode compartment.

With flow rates of 100 cc/min fuel and oxidant, the N₂ content of the anode exhaust is monitored by gas chromatography.* The response of the gas chromatograph to the anode exhaust sample is compared with the response to a standard of similar composition in order to determine the N₂ content. These measurements are made with both electrodes at atmospheric pressure, and again with the anode at atmospheric pressure and the cathode at 1 kPa above atmospheric pressure. The amount of N₂ measured varies considerably with the fuel flow rate, as the N₂ becomes diluted at higher flow rates; consequently, the fuel flow rates must be identical. Also, the differential pressure across the tile must be identical since a differential pressure can induce (or increase) cross-leakage of oxidant into the fuel.

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*The gas chromatographic methodology was developed with the assistance of M. Homa, ANL Analytical Chemistry Laboratory.

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