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ADVANCED FUEL CELL DEVELOPMENT

Progress Report for
October—December 1978

by

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

U of C-AUA-USDOE

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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CHEMICAL ENGINEERING DIVISION
ADVANCED FUEL CELL DEVELOPMENT
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ABSTRACT

This report describes advanced fuel cell research activities at Argonne National Laboratory during the period of October-December 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. Current electrolyte structures are comprised of LiAlO_2 particles and an eutectic of Li_2CO_3 and K_2CO_3 . The development of procedures for synthesizing LiAlO_2 from low cost materials is being pursued. The thermal stability of cold-pressed pellets of LiAlO_2 and carbonate eutectic has been tested at 925 K for 22 to 2400 h in air, CO_2 , and $\text{H}_2\text{-CO}_2\text{-H}_2\text{O}$. In general, under these test conditions, the allotropic form of the LiAlO_2 particles remained stable, but their surface area decreased with time of heat treatment. Thermo-mechanical tests indicated that the strength of LiAlO_2 pellets increases with increased particle surface area.

Several small (94 cm^2) cells have been operated in which the electrolyte tiles contained alkali carbonates and LiAlO_2 , primarily the γ allotrope. The performance of these cells was improved by using a high carbonate content (69 vol %) in the tiles and the mechanical strength of the tiles was improved by the use of a metal screen.

SUMMARY

Electrolyte Development

Experiments were conducted to determine the effect of temperature (775 to 975 K for 23-30 h in air) and reactant composition on the synthesis of LiAlO_2 from physical mixtures containing LiOH , Li_2CO_3 , K_2CO_3 , and $\text{Al}(\text{OH})_3$ or $\gamma\text{-Al}_2\text{O}_3$. Conditions are being sought that will promote the formation of small γ - and β - LiAlO_2 particles with high surface areas. The results of these experiments indicated that (1) the amount of β - LiAlO_2 with respect

to that of γ -LiAlO₂ in the product is increased as the equivalent fraction of lithium in the reactants is decreased, and (2) the relative amount of γ -LiAlO₂ in the product is increased and the BET surface area decreased as the heat-treatment temperature is increased from 775 to 975 K.

The thermal stability of pellets containing LiAlO₂ (α , β , or γ) and carbonate is being investigated. The BET surface areas of the three allotropic forms of LiAlO₂ used in these pellets were as follows: 75 and 26 m²/g for α -LiAlO₂, 40 and 12 m²/g for β -LiAlO₂, and 17 and 10 m²/g for γ -LiAlO₂. For these thermal stability tests, the pellets were heat treated at 925 K for 22 to 2400 h in air, H₂-CO₂-H₂O, and CO₂. After 2400 h of heat treatment, the α -LiAlO₂ pellets with a BET surface area of 75 m²/g partially transformed to γ -LiAlO₂ in air and H₂-CO₂-H₂O, but not in CO₂. In addition, the β -LiAlO₂ pellets with a BET surface area of 40 m²/g partially transformed to γ -LiAlO₂ after 2400 h in air, but not in H₂-CO₂-H₂O or CO₂. The γ -LiAlO₂ and other β -LiAlO₂ pellets did not undergo allotropic transformation under the conditions tested. Particle growth was most drastic with the α -LiAlO₂ pellets, where surface areas were reduced from the initial values of 75 and 25 m²/g to <5 m²/g within 1000 h. For the β -LiAlO₂ samples, the particle surface area decreased from 40 to 13 m²/g and 12 to 5 m²/g in 1000 h in all three gases; no further significant decrease in surface area occurred over the next 1400 h. The γ -LiAlO₂ pellets heat treated for 2400 h in H₂-CO₂-H₂O and CO₂ showed no significant change in surface area; in air, the surface area of the 17 m²/g sample exhibited no change at 1000 h, but decreased to <1 m²/g within 2400 h.

Component Analysis and Development

Measurements of instantaneous creep and permanent structural deformation were made on electrolyte mixtures containing LiAlO₂ and 55 wt % carbonate. The data indicate that, for any given allotropic form, the amount of instantaneous creep and structural deformation is inversely related to the surface area of the LiAlO₂ particles. Thermomechanical measurements were made on two pellets--one with clump-shaped α -LiAlO₂ particles having surface areas of 78 and 11 m²/g, and the other with clump-shaped α -LiAlO₂ particles having a surface area of 78 m²/g and rod-shaped β -LiAlO₂ particles having a surface area of 13 m²/g. These measurements indicated that rod-shaped particles decrease the mechanical strength of the pellet. Finally, preliminary creep measurements were made of pellets containing 14 m²/g γ -LiAlO₂ and 6 to 46 vol % carbonate which were maintained at 925 K for 100 h; these measurements showed an instantaneous creep of 0 to 1%.

At the request of the Fuel Cell Branch of DOE, we are conducting a survey of the literature on the aging and degradation of electrodes in molten carbonate fuel cells; this survey is expected to determine whether applied research leading to improvements in structural stability and corrosion resistance is needed in support of molten carbonate fuel cell commercialization. A search of the literature is under way, and relevant information is being collated.

Cell Tests

Three cells were operated in which the electrolyte tiles contained primarily γ -LiAlO₂ (with some β -LiAlO₂) as the matrix. Two of the cells (SQ-6 and -7) contained 55 wt % (61 vol %) alkali carbonate in the tile, and the performance of these cells was poor due to inadequate electrode wetting. The third cell contained 62.5 wt % (69 vol %) alkali carbonates in the tile, and its performance was significantly better due to improved electrode wetting. The incorporation of a Kanthal screen in the tiles of Cells SQ-6, -7 and -8 has improved the mechanical strength of the electrolyte tiles and reduced reactant gas cross-leakage. Expansion of the cathode in Cells SQ-6, -7 and -8 during *in situ* oxidation disrupted mating of the tile with the cathode housing and caused low wet-seal efficiencies. Oxidation of the cathode prior to cell assembly is recommended.

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 objective of the electrolyte development effort at ANL is to develop methods to synthesize LiAlO_2 that provide electrolyte structures with high strength and conductivity as well as good retention of the Li_2CO_3 - K_2CO_3 electrolyte. Both $\gamma\text{-Al}_2\text{O}_3$ (Degussa, Type C) and $\text{Al}(\text{OH})_3$ (ALCOA, H-705) were used as the starting materials to synthesize LiAlO_2 ; the $\gamma\text{-Al}_2\text{O}_3$ is significantly more expensive than the $\text{Al}(\text{OH})_3$ ($\sim \$6.70/\text{kg}$ vs $\$0.57/\text{kg}$).

A. Synthesis of LiAlO_2

A series of experiments was conducted to determine the effects of temperature and reactant composition on the synthesis of LiAlO_2 in physical mixtures containing $\text{Al}(\text{OH})_3$, LiOH , Li_2CO_3 , and K_2CO_3 . The initial physical mixtures contained one mole each of $\text{Al}(\text{OH})_3$ and LiOH and either 0.3 mol K_2CO_3 , or 0.5 mol Li_2CO_3 , or 0.5 mol Li_2CO_3 -0.3 mol K_2CO_3 . These samples were heat treated in air at temperatures up to 975 K for 23-30 h to obtain a mixture of LiAlO_2 and carbonate salt; the allotropes and surface areas after heat treatment are summarized in Table 1.

Table 1. Synthesis of LiAlO_2 from Physical Mixtures of $\text{Al}(\text{OH})_3$, LiOH , Li_2CO_3 , and K_2CO_3

Sample No.	Composition, ^a mol		Experimental Conditions ^b		LiAlO_2 Physical Properties	
	Li_2CO_3	K_2CO_3	Temperature, K	Time, h	Surface Area, m^2/g	Allotrope
134-36	0	0.3	775	24	c	$\beta\text{-LiAlO}_2$ (major) $\gamma\text{-LiAlO}_2$ (v.v. minor)
134-40	0.5	0	775	24	c	$\beta\text{-LiAlO}_2$ (major) $\gamma\text{-Al}_2\text{O}_3$ or $\gamma\text{-LiAlO}_2$ (v.v. minor)
134-12	0.5	0.3	775	30	c	$\beta\text{-LiAlO}_2$ (major) $\gamma\text{-LiAlO}_2$ (minor)
134-39	0	0.3	875	24	16	$\beta\text{-LiAlO}_2$ (major) $\gamma\text{-LiAlO}_2$ (v. minor)
134-38	0.5	0	875	24	30	$\alpha\text{-LiAlO}_2$ (major) $\gamma\text{-LiAlO}_2$ (medium)
134-27	0.5	0.3	875	23	28	$\gamma\text{-LiAlO}_2$ (major) $\beta\text{-LiAlO}_2$ (medium) $\alpha\text{-LiAlO}_2$ (minor)
134-41	0	0.3	925	24	11	$\gamma\text{-LiAlO}_2$ (major) $\beta\text{-LiAlO}_2$ (major)
134-42	0.5	0	925	24	7	$\gamma\text{-LiAlO}_2$ (major) $\alpha\text{-LiAlO}_2$ (major)
134-30	0.5	0.3	925	23	16	α -, $\gamma\text{-LiAlO}_2$ (major) $\beta\text{-LiAlO}_2$ (v. minor)
134-29	0.5	0.3	975	23	7	$\gamma\text{-LiAlO}_2$ (major) $\alpha\text{-LiAlO}_2$ (medium)

^aOne mole of LiOH and one mole $\text{Al}(\text{OH})_3$ present in each sample.

^bAll samples heat-treated in air.

^cData not available.

It is apparent from the results in Table 1 that both the heat-treatment temperature and the carbonate composition of the starting reactant mixture have an effect on the allotrope of LiAlO_2 obtained. All three samples maintained at 775 K yielded $\beta\text{-LiAlO}_2$ as the major phase. In contrast, the major phase of LiAlO_2 differed for each of the three samples tested at 875 K, the major phases being $\alpha\text{-LiAlO}_2$ for the 0.5 mol Li_2CO_3 sample (134-38), $\beta\text{-LiAlO}_2$ for the 0.3 mol K_2CO_3 sample (134-39), and $\gamma\text{-LiAlO}_2$ for the 0.5 mol Li_2CO_3 -0.3 mol K_2CO_3 sample (134-27). In the three samples tested at 925 K, $\gamma\text{-LiAlO}_2$ was one of the major phases; in addition, a second major phase was found in each of the three samples-- $\alpha\text{-LiAlO}_2$ in the samples containing Li_2CO_3 (134-30 and -42) and $\beta\text{-LiAlO}_2$ in the samples containing only K_2CO_3 (134-41). The one physical mixture of LiOH , $\text{Al}(\text{OH})_3$, Li_2CO_3 and K_2CO_3 (sample 134-29) tested at 975 K produced $\gamma\text{-LiAlO}_2$ as the major phase, with $\alpha\text{-LiAlO}_2$ as a second phase.

The few surface area measurements made indicate that, as expected, a lower surface area is obtained from samples heated at a higher temperature. For example, the surface area of sample 134-27, which was tested at 875 K, was four times larger than that of sample 134-29, which was tested at 975 K. A scanning electron micrograph (SEM) of the LiAlO_2 particles obtained by maintaining a physical mixture of LiOH , $\text{Al}(\text{OH})_3$, Li_2CO_3 , and K_2CO_3 at 975 K for 23 h in air is shown in Fig. 1. Submicrometer sized particles of LiAlO_2 clumped together into agglomerates are evident in the SEM. The particle size and morphology shown in Fig. 1 are typical of that observed in all samples of LiAlO_2 listed in Table 1.

Fig. 1. Scanning Electron Micrograph of $\gamma\text{-LiAlO}_2$ (major phase) and $\alpha\text{-LiAlO}_2$ (medium phase) Obtained from Heating LiOH , $\text{Al}(\text{OH})_3$, Li_2CO_3 , and K_2CO_3 at 975 K for 23 h in Air (sample 134-29).

Samples containing a physical mixture of LiOH and Al(OH)₃ and no carbonate were tested at 875 and 975 K for 24 h in air. The major phases found in these samples were β -LiAlO₂ after heat-treatment at 875 K and γ -LiAlO₂ after treatment at 975 K. The BET surface areas of the LiAlO₂ were 21 m²/g and 10 m²/g, respectively. The particle size and morphology of the LiAlO₂ in these samples are similar to those shown in Fig. 1.

The results of the above study revealed several important findings. First, it is difficult to obtain a pure phase of γ -LiAlO₂ by heat-treating physical mixtures of LiOH and Al(OH)₃ in the presence of Li₂CO₃ and/or K₂CO₃. In the samples containing Li₂CO₃ heat-treated at high temperatures (925 and 975 K), the expected product of the reaction of γ -Al₂O₃ with LiOH is γ -LiAlO₂; however, a competitive reaction of γ -Al₂O₃ with Li₂CO₃ to form α -LiAlO₂ also occurs. In the samples without Li₂CO₃ heat treated at 875 and 925 K (134-39 and -42), no α -LiAlO₂ was detected by X-ray diffraction analysis.*

Our previous results (ANL-78-40, p. 13) indicated that Al(OH)₃ reacts slowly with LiOH to form LiAlO₂ at low temperatures (725 and 775 K). The major fraction of LiAlO₂ obtained in these samples probably is formed from the reaction of LiOH and γ -Al₂O₃, the latter compound being produced by the dehydration of Al(OH)₃. The dehydration of Al(OH)₃ to form γ -Al₂O₃ would increase the cost by about 11-15¢/kg, which is about a 20% increase over the price of Al(OH)₃ (estimate made by Mr. John Starr, ALCOA, Pittsburgh, PA). Therefore, it is reasonable to investigate the use of γ -Al₂O₃ as the starting material. Because the supply of Al(OH)₃ (H-705) from ALCOA in the future is uncertain, a more readily available form of Al₂O₃ will have to be considered. Future experiments will involve a continuation of our synthesis efforts using dehydrated Al(OH)₃, as well as examining alternative low-cost aluminas.

Tests at ANL have shown that cells with electrolyte tiles containing γ -LiAlO₂ and 55 wt % carbonate have lower performance than that of cells with tiles containing α -LiAlO₂ and 55 wt % carbonate. The lower performance in the former cells is believed to be due to their lower volume fraction of electrolyte (61 vs 67%), which results in electrodes that are too "dry" (*i.e.*, electrolyte take-up by electrodes is insufficient). To test this hypothesis, we synthesized an electrolyte mixture containing LiAlO₂ and 62.5 wt % Li₂CO₃-K₂CO₃, the electrolyte volume fraction being 69%. To synthesize this electrolyte mixture, a stoichiometric amount of LiOH and γ -Al₂O₃ (Degussa) was physically mixed with sufficient Li₂CO₃ and K₂CO₃ to yield a carbonate content of 62.5 wt % (after reaction to form LiAlO₂ is complete). The physical mixture was held at 775 K for 2 h in air, and then at 975 K for 16 h in air-CO₂. This synthesis procedure is similar to one previously used to obtain an electrolyte mixture containing γ -LiAlO₂ and 55 wt % Li₂CO₃-K₂CO₃ (ANL-78-40, p. 7). However, in the sample containing 62.5 wt % carbonate, X-ray diffraction analysis after heat treatment showed that major phases of both β - and γ -LiAlO₂ were present. Figure 2 shows an SEM of this sample. The particle size ($\sim$ 0.2 μ m) and morphology (irregular bipyramids) appear similar to those obtained earlier in an electrolyte mixture containing γ -LiAlO₂ and 55 wt % carbonate (ANL-78-40, p. 8). The BET surface area is 26 m²/g, which

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

Fig. 2. Scanning Electron Micrograph of γ - and β - LiAlO_2 (both major phases) Obtained from a Physical Mixture of LiOH , $\gamma\text{-Al}_2\text{O}_3$, Li_2CO_3 , and K_2CO_3 Heated at 775 K for 2 h and 985 K for 16 h (sample no. 134-35).

is comparable to that of the $\gamma\text{-LiAlO}_2$ that is currently being obtained by the two-step heat treatment (775 and 975 K) of LiOH , $\gamma\text{-Al}_2\text{O}_3$ and 55 wt % $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$. The 62.5 wt % material will be pressed into tiles and tested. The above results indicate that the allotrope of LiAlO_2 obtained by heat treatment of physical mixtures of LiOH , $\gamma\text{-Al}_2\text{O}_3$, Li_2CO_3 , and K_2CO_3 is influenced by the amount of alkali carbonate present in the sample. A patent by Mason and Van Drunen (U.S. Patent 3, 998, 989, Dec. 21, 1976) claimed that the ratio of β - to $\gamma\text{-LiAlO}_2$ obtained in a reactant mixture of Al_2O_3 , Li_2CO_3 and K_2CO_3 varies with the amount of Li_2CO_3 and K_2CO_3 , the ratio of β - to $\gamma\text{-LiAlO}_2$ increasing as the Li_2CO_3 content was decreased. In our samples, the relative amount of Li_2CO_3 and K_2CO_3 remains constant. However, if the amount of lithium present in the sample as LiOH is considered, then the equivalent fraction of lithium (equivalents Li/equivalents Li plus equivalents K) is 0.73 in the sample containing 62.5 wt % carbonate and 0.76 in the sample containing 55 wt % carbonate. Perhaps the lower equivalent fraction of lithium in the sample containing 62.5 wt % alkali carbonate increases the relative amount of $\beta\text{-LiAlO}_2$ obtained. To test this hypothesis, we examined the relationship between the equivalent fraction of lithium and the allotropes of LiAlO_2 for the samples in Table 1; the results were consistent with the claims of Mason and Van Drunen and the above observations (*i.e.*, a higher equivalent fraction of lithium in the sample results in a higher ratio of $\gamma\text{-LiAlO}_2$ to $\beta\text{-LiAlO}_2$).

B. Thermal Stability of LiAlO_2

A comprehensive study is in progress on the thermal stability of α -, β - and γ - LiAlO_2 in the presence of carbonate at 925 K, the anticipated operating temperature of the molten carbonate fuel cell. For these tests, we determined the effects of time (22 to 2400 h) and gas environment (air, CO_2 , and 80% H_2 -20% CO_2 saturated with water at 295 K) on the stability of the allotropic form, size, shape, and surface area of heat-treated (925 K) LiAlO_2 particles. Changes in these properties affect the mechanical and electrolyte retention properties of the tile used in the molten carbonate fuel cell.

All tests were conducted with cold-pressed pellets (~ 1.3 -cm dia, ~ 0.8 -cm high) of 45 wt % LiAlO_2 (α , β , and γ) and 55 wt % carbonate (62 mol % Li_2CO_3 -38 mol % K_2CO_3); these pellets were 70-80% of theoretical density. The α - LiAlO_2 pellets consisted of porous clumps with a surface area of $75 \text{ m}^2/\text{g}$ or large chunks with surface areas of $26 \text{ m}^2/\text{g}$. The β - LiAlO_2 pellets consisted of aggregates of small particles or large rods with surface areas of 40 and $12 \text{ m}^2/\text{g}$, respectively. The γ - LiAlO_2 pellets consisted of small particles or large rods with surface areas of 17 and $10 \text{ m}^2/\text{g}$, respectively. All samples were characterized by X-ray analysis, scanning electron microscopy, and BET surface area analysis.

The BET surface areas reported were obtained by two types of experimental measurements: the first utilizes pressure data to obtain the adsorption isotherm of the sample; the second uses thermoconductivity of a helium sweep stream to obtain the desorption isotherm of the sample. Agreement between calculated surface areas for the two methods was usually within $\pm 20\%$. Extreme care had to be exercised in outgassing the LiAlO_2 samples prior to surface area measurement; samples were maintained at 180°C for >12 h to remove moisture.

1. Samples of α - LiAlO_2

The samples of $26 \text{ m}^2/\text{g}$ α - LiAlO_2 did not transform to γ - LiAlO_2 after 2400 h in any of the three gas environments. After 2400 h of testing, the samples of $75 \text{ m}^2/\text{g}$ α - LiAlO_2 did not transform to γ - LiAlO_2 in CO_2 , but partial transformation to γ - LiAlO_2 occurred in the air and H_2 - CO_2 - H_2O environments. From the data obtained to date, it appears that, in these two gas environments at 925 K, the α - to γ - LiAlO_2 transformation may be reversible. Additional tests are being initiated to verify these observations and to determine what factors are important in this process. In a previous study with powdered samples (ANL-78-71, p. 11), which transform faster than pellets, a sample of $75 \text{ m}^2/\text{g}$ α - LiAlO_2 transformed to γ - LiAlO_2 to a major extent after 22 h in air at 925 K and a sample of $26 \text{ m}^2/\text{g}$ α - LiAlO_2 did not. The transformation of α - to γ - LiAlO_2 is expected to be slowed when low-surface-area materials are used; however, some evidence of partial transformation should have been noted if this reaction occurs at a significant rate at 925 K in air.

Figure 3 shows the loss of surface area, which reflects the crystal growth that occurred in the α - LiAlO_2 cold-pressed samples, during the heat treatment in all three gas environments. Two different processes may be present as shown by the abrupt changes in slope of the curves in Fig. 3. During the first ~ 500 h, a drastic reduction in surface area occurs in the samples containing both the high- and low-surface area α - LiAlO_2 . Although

Fig. 3. Surface Area of α -LiAlO₂ During Heat Treatment at 925 K in Air, H₂-CO₂-H₂O, and CO₂.

the presence of CO₂ in the gas environment slows the surface-area decay somewhat, the final surface area of the LiAlO₂ samples is approximately the same in all three environments. After the surface area is <5 m²/g, crystal growth (*i.e.*, surface area decay) continues, but at a much slower rate. One would, therefore, expect that the BET surface area of α -LiAlO₂ in a electrolyte tile would be low in a fuel cell operated for >500 h.

Scanning electron micrographs were taken of the product obtained after heat treating 75 m²/g α -LiAlO₂ pellets at 925 K for 2400 h in all three gas environments. These photomicrographs showed bipyramids ranging in size from 0.1 to 5 μ m, there being no resemblance between the heated products and the original starting material. Scanning electron micrographs were also made of the products obtained after maintaining pellets of 26 m²/g α -LiAlO₂ at 925 K for 2400 h in air and H₂-CO₂-H₂O. These photomicrographs showed clusters of rounded bipyramids, 0.25 to 10 μ m in size, the products being appreciably different from the starting material and from the final products obtained from the pellets of 75 m²/g α -LiAlO₂.

2. Samples of β -LiAlO₂

The pellets containing 12 m²/g β -LiAlO₂ and carbonate did not undergo allotropic transformation after heat treatment for 2400 h at 925 K in all three gases. The pellets containing 40 m²/g β -LiAlO₂ and carbonate did not undergo allotropic transformation after heat treatment for 2400 h at 925 K in H₂-CO₂-H₂O or CO₂, but did show a minor amount of γ -LiAlO₂ when tested in air. Thus, there may be partial transformation of high-surface-area β -LiAlO₂ to γ -LiAlO₂ in an electrolyte tile of a fuel cell operated for more than 2400 h.

The curves presented in Fig. 4 depict the surface area losses during the heat treatment of the β -LiAlO₂ pellets. As can be seen in this figure, the 40 m²/g β -LiAlO₂ undergoes a rapid reduction in surface area in all three gases, to ~ 18 m²/g, in only 30 h. After this initial rapid loss, the surface area is reduced by only 20% over the next ~ 2000 h, from 18 to ~ 14 m²/g. The pellets of 12 m²/g β -LiAlO₂ also showed a slow rate of surface area reduction, having been reduced from 12 to 6 m²/g after 2400 h. These data indicate that, for the β -LiAlO₂ pellets, the final surface area is dependent on the initial surface area, and the gas environment does not significantly affect the surface area reduction.

Scanning electron micrographs of the products formed after heating the β -LiAlO₂ pellets for up to 2400 h in the three gases are similar to the SEM's of the original materials. After the heat treatment, fewer aggregates are present in the 40 m²/g β -LiAlO₂ material, which contains fine particles, many noticeably rod-shaped. The rods of the 12 m²/g β -LiAlO₂ sample may be slightly larger and wider, but this is not readily apparent on the SEM's.

Fig. 4. Surface Area of β -LiAlO₂ Samples During Heat Treatment at 925 K in Air, H₂-CO₂-H₂O, and CO₂.

3. Samples of γ -LiAlO₂

Figure 5 shows the surface area variation of the γ -LiAlO₂ pellets during the heat treatment. The mechanisms that produce the surface area changes exhibited by the 17 m²/g γ -LiAlO₂ in air are unexplained at present. After 2400 h of heat treatment, the micrograph of the 17 m²/g LiAlO₂ shows fairly large bipyramids, which have a much lower surface area than the original material. The product formed after 1000 h at 925 K in air had a surface area of 21 m²/g and consisted of bipyramids, some fairly large, covered with fine particles. One would have expected a lower surface area based on the appearance of this material. The appearance of the material produced after 22 or 318 h in air is identical to that of the original; however, the surface area of the LiAlO₂ after 22 h in air is more than twice as large as that of the original. This increase in surface area may be the result of a chemical reaction between the γ -LiAlO₂ and the gas environment.

In the other two gas environments (CO_2 and $\text{H}_2\text{-CO}_2\text{-H}_2\text{O}$), the surface area of the $17 \text{ m}^2/\text{g}$ $\gamma\text{-LiAlO}_2$ pellets remain unchanged from the original. The products, as seen in SEM's appear to be identical to the original material. For the $10 \text{ m}^2/\text{g}$ $\gamma\text{-LiAlO}_2$ pellets, the surface area was reduced slightly by heat treatment in all three gases. The microscopic appearance of all products after heat treatment for up to 2400 h was only slightly different from the original.

Fig. 5. Surface Area of $\gamma\text{-LiAlO}_2$ During Heat Treatment at 925 K in Air, $\text{H}_2\text{-CO}_2\text{-H}_2\text{O}$, and CO_2

In conclusion, the γ allotrope of LiAlO_2 continues to appear to be the most promising for long-term stable tiles, but the β allotrope also may be sufficiently stable. These tests indicate that $\alpha\text{-LiAlO}_2$ should not be used in electrolyte tiles because of its thermal instability.

III. COMPONENT ANALYSIS AND DEVELOPMENT

A. Thermomechanical Testing

Instantaneous creep (sudden thickness change at the eutectic melting temperature) and permanent structural deformation measurements were made on several electrolyte mixtures hot-pressed into small (12.5-mm dia) pellets. A high-sensitivity dilatometer was used to monitor the thermomechanical behavior of 11 pellets containing LiAlO_2 and 55 wt % Li_2CO_3 - K_2CO_3 (62 mol % Li_2CO_3 -38 mol % K_2CO_3) and one pellet containing LiAlO_2 and 62 wt % Li_2CO_3 - K_2CO_3 during several thermal cycles under a compressive stress of either 41 or 103 kPa. The procedure for thermal cycling was described in the last quarterly. The LiAlO_2 powders were characterized by X-ray diffraction analysis, BET surface area measurement, SEM, and particle size and size distribution analysis.

Table 4 is a summary of the instantaneous creep and permanent structural deformation for each pellet tested at a stress of 41 kPa. We had previously studied (ANL-78-95, p. 24) the effect of an increase in stress by a factor of 2.5 (41 to 103 kPa) on the instantaneous creep of LiAlO_2 pellets. The previous results indicated that an increase in the stress from 41 to 103 kPa does not affect the creep significantly for pellets made from LiAlO_2 particles with surface areas $>30 \text{ m}^2/\text{g}$; however, for pellets made with LiAlO_2 particles with surface areas between 30 and $\sim 17 \text{ m}^2/\text{g}$, the increase in creep values is nearly proportional to the increase in stress. Pellets made with LiAlO_2 powders with surface areas $<15 \text{ m}^2/\text{g}$ exhibit a large instantaneous creep ($> 50\%$) at a stress of 41 kPa. Because the current data are consistent with the previous results, only data obtained at a stress of 41 kPa are presented in Table 4. The data show that, as the surface area of the LiAlO_2 particles (α , β , and γ) in the pellets is increased, the amount of instantaneous creep and permanent structural deformation decreases.

Initial studies on pellets containing low-surface-area LiAlO_2 powders indicated that their thermomechanical properties are not affected by the particle shape. However, a pellet containing both rod and clump-shaped LiAlO_2 particles (surface area, $44 \text{ m}^2/\text{g}$) had a greater instantaneous creep and permanent structural deformation than pellets containing a single LiAlO_2 particle shape and comparable surface area. To explore this behavior further, thermomechanical tests were made on two pellets--one with clump-shaped LiAlO_2 particles (A-61 in Table 4) and the other with clump- and rod-shaped LiAlO_2 particles (A-62 in Table 4). As can be seen in Table 4, the creep and permanent deformation of sample A-62 was somewhat higher than that of A-61.

The effect of particle size and size distribution on the thermomechanical behavior of the pellets listed in Table 4 is difficult to assess. Although the average particle sizes of the LiAlO_2 powders are similar, pellets which typically have little creep or deformation generally had LiAlO_2 surface areas of $17 \text{ m}^2/\text{g}$ and a bimodal particle size distribution. Further thermomechanical tests are planned on several LiAlO_2 powders having approximately the same surface area but different particle size distributions in an effort to determine if the previously noted relationship is real or fortuitous.

Studies are under way to determine the effect of electrolyte concentration on thermal expansion and long-term creep (100 h). Preliminary creep tests (~ 925 K for 100 h) have been conducted on pellets containing low-surface-area γ - LiAlO_2 ($14 \text{ m}^2/\text{g}$) and a Li_2CO_3 - K_2CO_3 content ranging from 6-46 vol %; these pellets had very low creep rates, 0 to <1%.

Table 2. Instantaneous Creep and Permanent Structural Deformation at 41 kPa of Pellets Containing LiAlO_2

Pellet Identification	LiAlO_2 Allotrope	Particle Shape	Average Particle Size, μm	Surface Area m^2/g ($\pm 10\%$)	Pellet Thickness, mm	Instantaneous Creep (770 K), % Compression ^a	Structural Deformation, % Decrease ^a
A-151	α	clumps	0.92	22	3.2	3	7
B-123 (2 pellets)	β	clumps	5.9	11	3.5	>50	>50
B-169	β	clumps	1.5	22	3.2	1	4
B-120	β	clumps	b	30	5.7	<1	<1
G-29	γ	clumps	1.2	7	3.7	>50	>50
G-24	γ	clumps	1.1	14	3.8	>50	>50
A-61	α	clumps	0.96	49 ^c	3.8	3	4
A-62	50% α - 50% β	clumps & rods	1.0	50 ^d	3.1	8	9
G-35 ^e	50% γ - 50% β	clumps	1.18	26	3.9	<1	<1

^aPercent of original thickness.

^bData not available.

^cThis sample contains both high ($78 \text{ m}^2/\text{g}$)- and low ($11 \text{ m}^2/\text{g}$)-surface-area α - LiAlO_2 .

^dThis sample contains high ($78 \text{ m}^2/\text{g}$)-surface area α - LiAlO_2 clumps and low ($13 \text{ m}^2/\text{g}$)-surface-area β - LiAlO_2 rods.

^eThis sample contains 62.5 wt % carbonate, whereas the others have 55 wt % carbonates.

B. Electrode Aging in Molten Carbonate Fuel Cells

At the request of the Fuel Cell Branch of DOE, we surveyed the literature on the aging and degradation of electrodes in molten carbonate fuel cells. This survey is being conducted to determine whether applied research leading to improvements in electrode structural stability and chemical/electrochemical stability is needed in support of molten-carbonate fuel cell commercialization. This survey and contacts with investigators of fuel cell technology will serve as the basis for establishing the need for applied research, if the information will accelerate the commercialization of molten carbonate fuel cells. To date, computer searches of the relevant literature from the DOE/RECON and NASA/RECON files have been completed, and reports and publications are being collated. In addition, a search of the literature not included in the two above-mentioned files is under way.

IV. CELL TESTING

During this quarter, three cells (SQ-6, -7, and -8) were operated. The cell design was described in ANL-78-40, p. 29-30. The electrolyte tiles contained primarily γ -LiAlO₂, but also some β -LiAlO₂, prepared by reacting LiOH, Al₂O₃ (Degussa), Li₂CO₃, and K₂CO₃. These tiles were reinforced by a metal screen of Kanthal wire. In Cells SQ-6 and -7, the electrolyte mixture contained 55 wt % (61 vol %) alkali carbonates; the amount of alkali carbonates was increased to 62.5 wt % (69 vol %) in Cell SQ-8.

Parameters of cell construction for these three cells are given in Table 5; Cell SQ-3, which had shown the best performance to date in the present apparatus, is also presented. Cell performance data are shown in Fig. 6 for all four cells. The low performance of Cells SQ-6 and -7 has been attributed to inadequate electrode wetting by the alkali carbonates. The higher performance of Cell SQ-8 compared to that of Cells SQ-6 and -7 seems to have resulted from the increase in the amount of alkali carbonates in the electrolyte tile; however, the lower performance of Cell SQ-8 than that of SQ-3, both of which had about the same volume percent of alkali carbonates, is probably due to differences in the type of LiAlO₂ used in the electrolyte tile and/or to

Table 3. Cell Design Details

	SQ-3	SQ-6	SQ-7	SQ-8
Electrolyte Tile	Unreinforced	Reinforced ^a	Reinforced ^a	Reinforced ^a
LiAlO ₂ phase	α -LiAlO ₂ (major) γ -LiAlO ₂ (minor)	γ -LiAlO ₂ (major) β -LiAlO ₂ (minor)	γ -LiAlO ₂ (major) β -LiAlO ₂ (minor)	γ -LiAlO ₂ (major) β -LiAlO ₂ (major)
LiAlO ₂ surface area, m ² /g	78	26	26	26
Carbonate content, ^b wt % (vol %) ^c	55(68)	55(62)	55(62)	62.5(69)
Thickness, cm	0.20-0.22	0.20-0.21	0.20-0.22	0.19-0.22
Anode				
Thickness, cm	0.051	0.064	0.051	0.072
Mean pore diameter, μ m	5.9	10.5	7.3	8.5
Porosity, %	68.9	74.6	74.0	73.9
Cathode ^d				
Thickness, cm	0.061	0.064	0.064	0.064
Mean pore size, μ m	6.4	10.5	10.2	10.2
Porosity, %	70.2	74.6	73.1	73.1

^aKanthal, Type A-1 screen reinforcement.

^b62 mol % Li₂CO₃-38 mol % K₂CO₃.

^cBased on carbonate density at 650°C of 1.94 g/cm³ and LiAlO₂ densities of 2.60 for γ - and β -LiAlO₂ and 3.40 g/cm³ for α -LiAlO₂.

^dCharacteristics prior to *in situ* oxidation.

differences in the electrodes. In addition, the better performance of Cell SQ-3 probably indicates that its electrodes were wetted better by the electrolyte. We believe that the performance of cells containing primarily γ - LiAlO_2 can be improved further by two design changes: increasing the amount of alkali carbonates in the electrolyte tile above 69 vol % and by decreasing the mean pore size of either one or both of the electrodes. Future cell tests will investigate these design changes. At this time, it appears that we will achieve reasonable cell performance with the type of LiAlO_2 used in Cells SQ-6, -7 and -8. The mechanical strength of the reinforced electrolyte tiles after testing in Cells SQ-6, -7 and -8 was significantly greater than that of unreinforced tiles tested in previous cells. Also, cross-leakage of reactant gases was decreased by reinforcement of the tile. Condensation of water in the cathode exhaust, which is a clear indication of cross-leakage of fuel into the oxidant stream, occurred in each of the cells with unreinforced tiles, but not in any of the cells with reinforced tiles.

Operation of Cells SQ-6, -7 and -8 indicated that cathode expansion (by 0.18 to 0.23 mm) during *in situ* oxidation interferes with formation of an adequate wet seal between the tile and the cathode housing. Each of these cells had been assembled such that the clearance between the unoxidized cathode and the tile was 0.06 to 0.11 mm, thereby allowing a seal to form between the tile and housing during cell startup. However, when the cell temperature reached approximately 900 K, the seal was lost and then gradually reformed with continued operation. The maximum cathode wet-seal efficiency* in each of these cells did not exceed 97%, and was always less than the anode wet-seal efficiency. The cathode expansion during *in situ* oxidation appeared to disrupt mating of the tile with the cathode housing, thereby preventing formation of an adequate cathode wet-seal. This problem could be eliminated by providing a greater initial clearance, but a more attractive solution would be to oxidize the cathode prior to cell assembly; this would diminish changes in the pore structure of the cathode during cell operation.

Fig. 6. Performance of Cells SQ-3, -6, -7 and -8

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

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