

Particle growth behaviour of LiAlO_2 containing ZrO_2 in Li/Na carbonate electrolytes

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Abstract

The growth of particles of lithium aluminate (LiAlO_2) as an electrolyte retention material in molten carbonates leads to a decrease in the electrolyte retention ability, and so the performance of the fuel cell deteriorates. We have studied how to improve the material in order to maintain the electrolyte retention ability for a long term in Li/Na carbonates. As a result, we found that zirconia powder added to lithium aluminate keeps the electrolyte retention ability constant for over 7000 h in the alkaline carbonate in a $P_{\text{CO}_2} = 0.1$ atmosphere. © 1998 Elsevier Science S.A.

Keywords: Alkaline carbonate; Electrolyte retention material; Lithium aluminate

1. Introduction

Lithium aluminate (LiAlO_2) has been normally used as an electrolyte retention material in molten carbonate fuel cells (MCFCs). The particles of LiAlO_2 have been grown for long term cell operation. This growth of particles leads to a decrease in the electrolyte retention ability [1]. Therefore, the performance of the fuel cell deteriorates. This phenomenon is one of the principal causes of the deterioration of MCFCs. We have studied how to improve the material in order to maintain the electrolyte retention ability for a long term in Li/Na carbonates. We have reported that zirconia powder added to LiAlO_2 is effective in maintaining the electrolyte retention ability in Li/K carbonates under a 30% CO_2 /70% air atmosphere [1]. In this paper, we have evaluated the electrolyte retention ability of this material, not only in the Li/K carbonate, but also in the Li/Na carbonate under various atmospheric conditions in terms of the

BET specific surface area and by using the scanning electron microscope (SEM). Furthermore, we constructed single cells using the improved material and evaluated the cells performance.

2. Experimental

2.1. Component tests (out-of-cell tests)

The apparatus used for the component test is shown schematically in Fig. 1. We used the Li/K (62:38 m/o) carbonate and Li/Na (52:48 m/o) carbonate for the electrolyte (these eutectic carbonates were made by Rasa Industries). The electrolyte retention material used are $\gamma\text{-LiAlO}_2$ (manufactured by the Foote Mineral Company, HSA-10), ZrO_2 (made by Nacalai Tesque Inc.) and a $\text{LiAlO}_2 + \text{ZrO}_2$ mixture. The $\text{LiAlO}_2 + \text{ZrO}_2$ mixture was made by using a ball milling method. The alkaline carbonate was mixed with 33 wt% of these electrolyte retention materials. This mixture was put into an alumina crucible, which was placed inside an outer stainless steel container. This mixture was heated to 923 K

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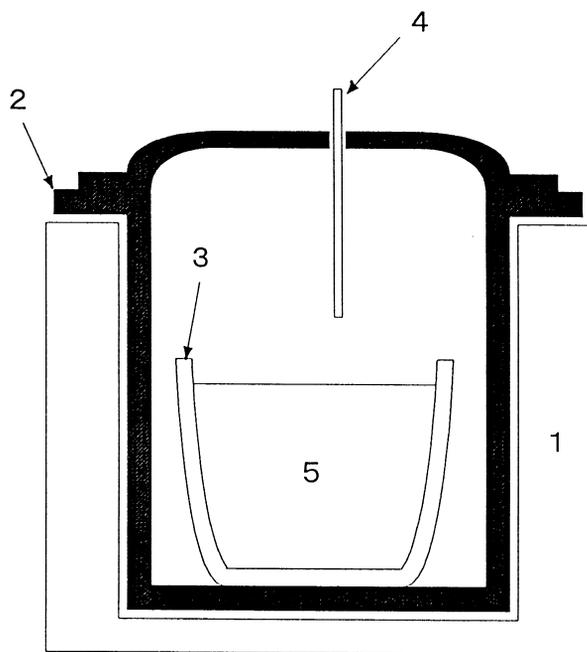


Fig. 1. Schematic view of apparatus for component tests. 1, electric furnace; 2, stainless steel container; 3, alumina crucible; 4, alumina gas supplying tube; 5, electrolyte and electrolyte retention materials.

and operated in an electric furnace under various CO_2 concentration atmospheres ($\text{CO}_2/\text{air} = 0:100, 10:90, 20:80, 30:70$ vol%). The mixture was sampled at regular intervals. The samples were neutralized with a solution of acetic acid, acetic anhydride and ethanol and then drying them, the BET specific surface areas of these materials were measured using Flow Sorb II-2300 (Micromeritics) and we observed the samples by a scanning electron microscope (Hitachi, S5000).

2.2. Cell tests

Single cells using the developed electrolyte retention

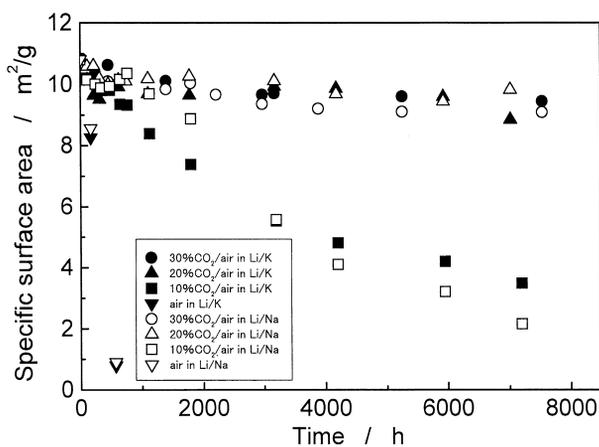


Fig. 2. Changes in surface area of LiAlO_2 in Li/K and Li/Na carbonate under various concentrations of CO_2 at 923 K.

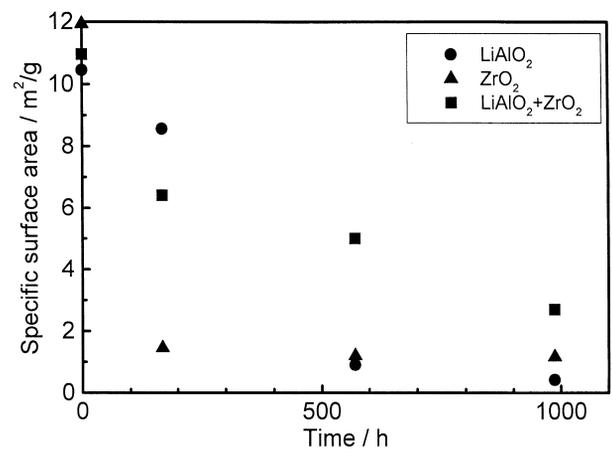


Fig. 3. Changes in surface area of various electrolyte retention materials in Li/Na carbonate in an air atmosphere at 923 K.

material were constructed using a combined technology [2]. We used the $\text{LiAlO}_2 + \text{ZrO}_2$ mixture as the electrolyte retention material. The electrolyte used was Li/K (62/38 m/o) carbonate. For the anode, the Ni-5% Al (Nippon Atomized Metal Powders Co.) coated with alumina particles (Degussa aluminium oxide C) was used and nickel (Inco type 255) was used for the cathode. The cells, which were operated for a long period, were evaluated for the rate of voltage decay.

3. Results

It is well known that the CO_2 concentration of cathode gas is less than 30% during cell operation. With this in mind, we carried out the measurement under various CO_2 concentration atmospheres. Fig. 2 shows the changes in the specific surface area of LiAlO_2 in alkaline carbonates as a function of the CO_2 concentration. The changes in the specific surface area of LiAlO_2 were almost the same in both

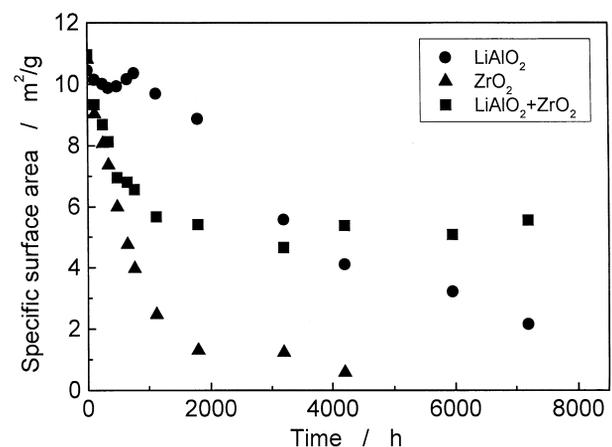


Fig. 4. Changes in surface area of various electrolyte retention materials in a Li/Na carbonate under 10% CO_2/air atmosphere at 923 K.

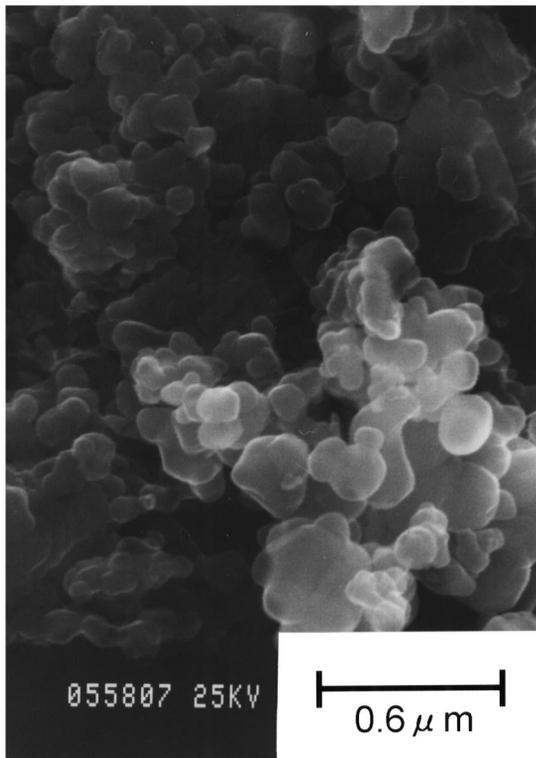


Fig. 5. SEM photograph of LiAlO_2 before test.

Li/K and Li/Na carbonates. The specific surface areas decreased as the time proceeded and as the CO_2 con-

centration decreased. These results agree with the reference [3].

Next, we investigated the zirconia powder added to LiAlO_2 for the electrolyte retention material. Fig. 3 shows the changes in the specific surface area of LiAlO_2 , ZrO_2 , and $\text{LiAlO}_2 + \text{ZrO}_2$ in Li/Na carbonate in an air atmosphere. The specific surface area of LiAlO_2 and ZrO_2 at 570 h was about $0.9 \text{ m}^2/\text{g}$ and $1.2 \text{ m}^2/\text{g}$, respectively. On the other hand, the specific surface area of $\text{LiAlO}_2 + \text{ZrO}_2$ at 570 h was about $5.0 \text{ m}^2/\text{g}$. The addition of ZrO_2 to LiAlO_2 is very effective in maintaining the specific surface area in Li/Na carbonate. This tendency was similar to the Li/K carbonate.

Fig. 4 shows the changes in the specific surface area of these materials in the Li/Na carbonate under 10% CO_2 /90% air atmosphere. The specific surface area of the $\text{LiAlO}_2 + \text{ZrO}_2$ is higher than the LiAlO_2 over 4000 h and is very stable.

Next, we observed the microstructures of LiAlO_2 and $\text{LiAlO}_2 + \text{ZrO}_2$ by SEM. Fig. 5 shows the SEM photograph of LiAlO_2 before the test. The mean size of the particles is about $0.1 \mu\text{m}$ in this photograph. Though the mean size of only the zirconia particles before testing was just a few μm , this ZrO_2 has many pores, so the specific surface area was about $11 \text{ m}^2/\text{g}$. The microstructure of $\text{LiAlO}_2 + \text{ZrO}_2$ before the test is almost the same as LiAlO_2 . Fig. 6(a),(b) shows the SEM photographs of LiAlO_2 after 987 h in a Li/Na carbonate in an air atmosphere. We can see that the particle of LiAlO_2 grew up to the mean size of about $10 \mu\text{m}$. The SEM

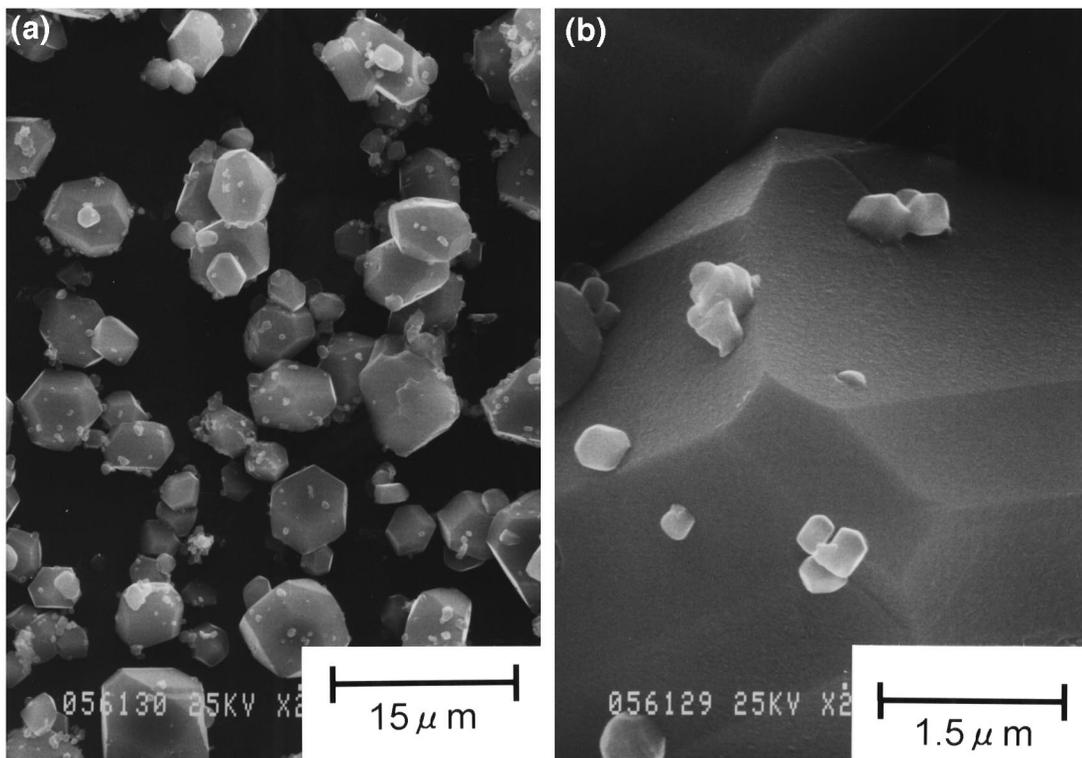


Fig. 6. (a),(b) SEM photograph of LiAlO_2 after 987 h in Li/Na carbonate in an air atmosphere.

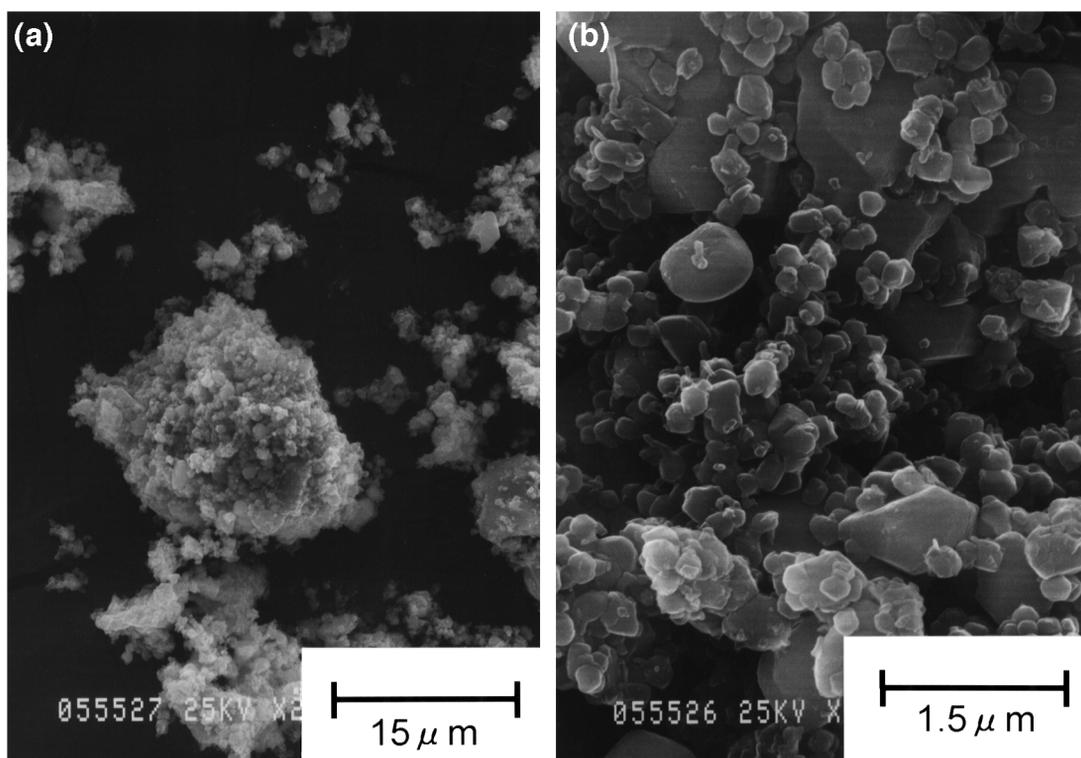


Fig. 7. (a,b) SEM photograph of $\text{LiAlO}_2 + \text{ZrO}_2$ after 987 h in Li/Na carbonate in an air atmosphere.

photographs of $\text{LiAlO}_2 + \text{ZrO}_2$ after 987 h under the same conditions are shown in Fig. 7(a),(b). In these cases, particle grew more slowly compared with only LiAlO_2 . These microstructures reflect the results of the surface area measurement.

We constructed the single cell using $\text{LiAlO}_2 + \text{ZrO}_2$ for the electrolyte retention material and tested it. The performance of this cell kept almost constant up to 2500 h, as shown in Fig. 8.

Two mechanisms are considered in the particle growth of LiAlO_2 . One is the solid state sintering mechanism, which is where the particles react with each other in an alkaline carbonate and grow during long term operation. The other is the dissolution-deposition mechanism, which is where the particle grows when LiAlO_2 dissolves and deposits in the alkaline carbonates. It seems that the two mechanisms are related in a complicated way. If the particle growth of LiAlO_2 occurs mainly by the dissolution-deposition mechanism, the particle size of LiAlO_2 should be about the same, regardless of the addition of ZrO_2 . But the particle size of LiAlO_2 was not same as $\text{LiAlO}_2 + \text{ZrO}_2$ in our results. Our results suggested that the addition of ZrO_2 to the LiAlO_2 prevented the particle growth of LiAlO_2 . It seems that the fine ZrO_2 particles cover most parts of the LiAlO_2 surface. Now we have applied the fine ZrO_2 powders (mean particle size: $0.25 \mu\text{m}$) to electrolyte retention materials. Therefore, we considered that the particle of LiAlO_2 grew by not only the dissolution-deposition mechanism but also the solid state sintering mechanism

and we found that ZrO_2 powder added to LiAlO_2 is effective in maintaining the electrolyte retention ability.

4. Conclusions

The electrolyte retention ability of LiAlO_2 , ZrO_2 and $\text{LiAlO}_2 + \text{ZrO}_2$, not only in Li/K carbonates, but also in Li/K carbonates under various atmospheric conditions was investigated. We found that zirconia powder added to lithium aluminate has a high electrolyte retention ability compared with an only lithium aluminate. Our results suggested that the particle of LiAlO_2 grew by not only the

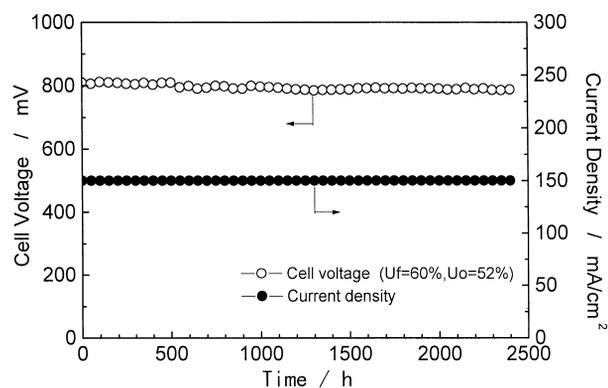


Fig. 8. Performance of a single cell using ZrO_2 added to LiAlO_2 for the electrolyte retention material in Li/K carbonate.

dissolution-deposition mechanism but also the solid state sintering mechanism.

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