Durable MCFC Electrolyte Plate Consisting of α - and β -LiAlO₂

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The stability of rod-shaped β -phase lithium aluminate was tested to evaluate its suitability for use as a reinforcing material for α -phase lithium aluminate electrolyte plates. In contrast to previous reports, the β -phase which was added to the α -phase remained stable at 750°C. Our study confirmed that there was a difference in allotropic transformation between β -phase with α -phase and β -phase with γ -phase. The electrolyte plate consisting of β -phase with α -phase showed an obvious improvement of the rate of pore coarsening at 650°C in an atmosphere containing steam. This suggests that a combination of α -phase and β -phase will be an effective substitute for currently used MCFC electrolyte plate materials.

1 INTRODUCTION

It is well known that pore coarsening of electrolyte plates is one of the main factors responsible for molten carbonate fuel cell (MCFC) deterioration. There are many previous studies¹⁻³⁾ which show that it is caused by the growth of lithium aluminate particles and driven by the "dissolution - deposition" mechanism in molten carbonate electrolyte. In order to inhibit this phenomenon, we proposed an α -phase lithium aluminate retaining material instead of the previously used γ -phase material⁴⁾. The α -phase powder has a slightly larger particle size and a lower level of agglomeration relative to the previously used γ -phase powder. Electrolyte plates which consist only of retaining material are, however, thought to have poor fracture resistance, especially at thermal cycling during cell operation.

In this study, we tested the stability of rod-shaped β -phase lithium aluminate to evaluate its suitability for use as a reinforcing material for α -phase retaining material in electrolyte plates.

According to a previous report¹⁾, the allotropic transformation of the rod-shaped β -phase in an alkali carbonate environment at temperatures above 700°C resulted in the disappearance of the rod-shape. However, in the case of a mixture with α -phase retaining material, there are no known studies on the stability of rod-shaped β -phase beyond 700°C. Therefore, the stability of the β -phase at 750°C was first examined in order to characterize the difference in allotropic transformation between the β -phase with α -phase and β -phase with γ -phase. The difference in the rate of pore coarsening at 650°C between the β -phase with α -phase sample and the previously used γ -phase sample was also examined. The allotropic phase stability and structural stability of these samples are discussed in this paper.

2 EXPERIMENTAL

2.1 Powder preparation

The α -phase lithium aluminate powder was obtained by heat treatment of that of fine powder. The rod-shaped β -phase lithium aluminate powder was synthesized from γ -alumina, lithium hydroxide and sodium hydroxide^{5,6)}. Commercially available γ -phase lithium aluminate powder (Foote Mineral Company, HSA-10) was used.

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2.2 Matrix fabrication

Three types of electrolyte plate matrices were fabricated. Type A consisted of 70 wt% α -phase and 30 wt% rod-shaped β -phase. Type B consisted of 70 wt% γ -phase and 30 wt% rod-shaped β -phase. As a reference, we also prepared type C, which consisted entirely of γ -phase.

2.3 Out-of-cell test

The sample matrices were impregnated in alkali carbonate in a molar ratio of Li:K=62:38. Then they were heated in a controlled gas environment (CO_2 30%, steamed at 80°C , balance air) in a gold crucible. After these tests, all the samples were washed

Fig. 1 X-ray diffraction pattern after 2000 h of the test on the type A matrix.

Fig. 2 X-ray diffraction pattern after 2000 h of the test on the type B matrix.

Type A

using a mixture of acetic acid and acetic anhydride. Then they were analyzed using an SEM (JSM-5400LV; JEOL), an X-ray diffractometer (RINT-1200, Rigaku) and mercury porosimeter (Poresizer 9320, Shimadzu).

3 RESULTS AND DISCUSSION

Figures 1 and 2 show X-ray diffraction patterns after 2000 h of the out-of-cell test at 750°C for the type A and type B matrices, respectively. We can see β -phase peaks after 2000 h of the test in the type A matrix. On the contrary, in the case of the type B matrix, the peaks of the β -phase almost disappeared after the test. This result indicates that the β -phase was completely transformed into γ -phase during the test in the type B matrix. Figure 3 shows SEM pictures after 2000 h of the test for the type A and type B matrices. A clear difference in particle shape between the type A and type B samples can be seen. In the type B sample, the aspect ratio of the rod-shaped β -phase particles was reduced, while the β -phase particles clearly retained their rod-shape in the type A sample. This suggests that the β -phase, which is surrounded by the α -phase, is sufficiently stable in alkali carbonate even at 750°C . It has been shown previously that the γ -phase is more stable than the β -phase at 750°C in alkali carbonate¹⁾. However, a certain stimulation is also required for actual allotropic transformation from β -phase to γ -phase. The crystal structure of the β -phase is orthorhombic,

Type B

Fig. 3 SEM pictures after 2000 h of the test on the type A and type B matrices. (750°C , CO_2 30%).

and is akin to that of the γ -phase which is tetragonal⁷⁾. Because of their similarity, a β -phase particle which is surrounded by the γ -phase (as shown in Fig. 4(a)) is affected by the stable γ -phase, and this influence stimulates the transformation from the β -phase to the γ -phase. On the other hand, the crystal structure of the orthorhombic β -phase is dissimilar to that of the α -phase, which is hexagonal. Therefore, the β -phase which is surrounded by the α -phase (as shown in Fig. 4(b)) is not be influenced by the α -phase and

Fig. 4 Schematic model of the stimulation effect for β -phase transformation. (750°C , CO_2 30%).

Fig. 5 X-ray diffraction patterns before the test and after 5500 h of the test on the type C matrix.

Without steam

With steam

Fig. 6 SEM pictures after 5500 h of the test on the type C matrix. (650°C , CO_2 30%).

remained pseudo stable even at 750°C . Along with the previous results, which indicate a stable β -phase up to 700°C , it is suggested that the β -phase reinforcement in the matrix would be a suitable measure for larger size cell operation, in which a temperature gradient beyond 700°C is conceivable.

In the second part of our study, the structural stability of the type A matrix at 650°C was tested relative to the type C matrix. In the case of MCFCs, previous reports indicate an acceleration effect on particle growth in an atmosphere containing steam³⁾. Figure 5 shows the X-ray diffraction patterns of type C matrix before and after 5500 h of the test. It is obvious there are some peaks of the α -phase after the test, regardless of the presence of steam. The α -phase peaks at around 19° and 45° became higher in the presence of steam. Figure 6 shows SEM pictures of the type C matrix after 5500 h of the test. We can see a clear difference between the sample which was subjected to steam and that which was not. It is obvious that the rate of particle growth is faster in the presence of steam. Similar to previous results³⁾, these experimental results indicate that the presence of steam accelerates particle growth and α -phase formation due to activation of the "dissolution - deposition" mechanism. Figure 7 shows X-ray diffraction patterns of the type A matrix before and after 5500 h of the test in the presence of steam. Contrary to the results of the type C matrix, there were no significant differ-

ences between before and after the test. Thus we can see that the β -phase with α -phase remained stable. Figure 8 shows SEM picture of the type A matrix after 5500 h of the test in the presence of steam. As can be seen in this picture, there is no significant particle growth even in the presence of steam, whereas there was apparent particle growth in the case of the type C matrix. Figure 9 shows change of average pore diameter during the test for the type A and type C samples. The type A matrix

Fig. 7 X-ray diffraction pattern before the test and after 5500 h of the test on the type A matrix.

Fig. 8 SEM picture after 5500 h of the test on the type A matrix. (650°C, CO₂ 30% with steam).

Fig. 9 Pore diameter change differences between the type A and type C matrices.

showed a lower rate of pore coarsening than type C in the 5500 h test. These experimental results indicate that the type A matrix is structurally stable relative to the type C matrix at 650°C in the presence of steam. The “dissolution - deposition” activity of combination of α -phase and β -phase was therefore thought to be lower than that in the case of the γ -phase.

4 CONCLUSION

The experimental results indicate that there is a clear difference in allotropic transformation between β -phase with α -phase and β -phase with γ -phase. The β -phase is sufficiently stable with α -phase even at 750°C. We concluded this difference in allotropic combination affected β -phase stability. In addition, electrolyte plates which consist of the α -phase and rod-shaped β -phase have a lower rate of pore coarsening at 650°C in the presence of the steam than electrolyte plates which consist of γ -phase. These results suggest that the combination of α -phase retaining powder and β -phase reinforcing powder will be an effective substitute for currently used MCFC electrolyte plate materials.

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