Short communication

Effective fabrication method of rod-shaped γ-LiAlO$_2$ particles for molten carbonate fuel cell matrices

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Abstract

An effective fabrication method for rod-shaped γ-LiA1O$_2$ particles for molten carbonate fuel cell matrices via the synthesis of porous β-LiAlO$_2$ agglomerates that are easily washed and dispersed with deionized water has been investigated. In order to make large pores and high porosity in the reaction mixture, powder types of carbon and ammonium carbonate that make little ash and undesired material during the whole process are utilized. Regardless of the kind of pore-formers used, most of the rod-shaped β-/γ-LiAlO$_2$ particles are 1 μm in diameter and 10–15 μm long (aspect ratio of 10–15). The crystal structure of rod-shaped γ-LiAlO$_2$ particles synthesized from the reaction mixture with pore-formers coincides exactly with that of commercial γ-LiAlO$_2$ powders. As a consequence, cell performance using rod-shaped γ-LiAlO$_2$ particle reinforced matrices is highly improved in comparison with non-reinforced standard matrices.
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1. Introduction

The molten-carbonate fuel cell (MCFC) has attracted special interest as a device for electric power generation. MCFCs have potentially many advantages, including very high electrochemical conversion efficiency, safety, and pollution-free operation. Nevertheless, many improvements in the longevity and the efficiency of MCFCs are still required for the commercialization of this technology. The primary challenge is the construction of a fuel cell stack of component materials that operates at temperatures of about 650 °C. Also, any matrix containing very reactive electrolytes, such as molten carbonates, should be inert and stable for electrolyte retention [1,2]. Until now, MCFCs have displayed large changes in the volume in of matrix during thermal cycling of the electrolyte. These temperature fluctuations create stresses that produce microcracks and morphology changes in the electrolyte matrix [2,3].

The above structural weaknesses were eliminated when Hyun et al. [3,5] used rod-shaped γ-LiAlO$_2$ as a matrix material to support the liquid electrolyte [3,5]. The chemical and thermal stability and mechanical strength enabled this matrix to be stable under the atmospheric pressures and temperatures typical of the operating conditions of MCFCs [4,6,7]. The fabrication of rod-shaped γ-LiAlO$_2$ particles is time-consuming, however, since the agglomerates of the intermediate products (rod-shaped β-LiAlO$_2$ particles) are difficult to wash and disperse with deionized-water.

This study reports an effective fabrication method for rod-shaped γ-LiAlO$_2$ particles for molten carbonate fuel cell matrices, via the synthesis of porous β-LiAlO$_2$ agglomerates that are easily washed and dispersed with deionized-water. The matrices are fabricated by tape casting, and their performance in single-cell tests.

2. Experimental

The overall experimental flow chart for this study is given in Fig. 1, and the detailed experimental procedure in each step is outlined below.

The following fabrication method of rod-shaped β-/γ-LiAlO$_2$ particles has been suggested by Hyun et al. [3,5,8,9];

$$2LiOH + Al_2O_3 = 2LiAlO_2 + H_2O \qquad (1)$$
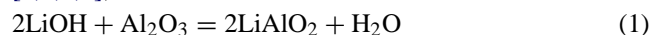
LiOH·H$_2$O (Junsei Co.) and γ-Al$_2$O$_3$ (A Johnson Mathey Co.) were used as sources of LiOH and A1$_2$O$_3$, respectively, and NaOH (Junsei Co.) was used as a flux and reaction
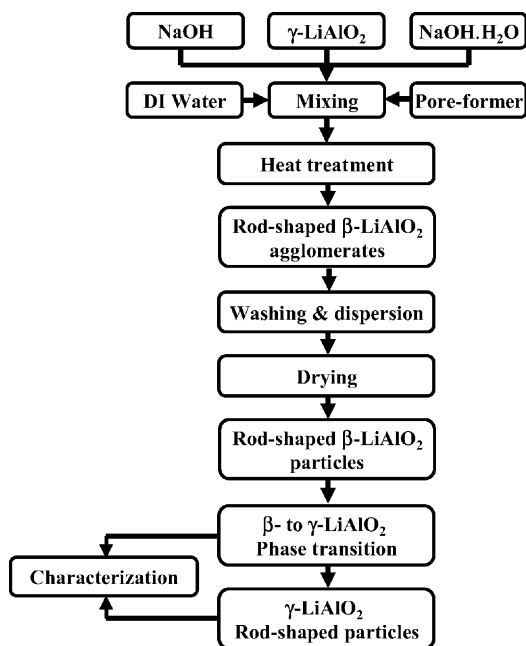
Fig. 1. Overall experimental flow chart.

promoter. Carbon powder (YP-17, Cray Chemical Co.) and $(NH_4)_2CO_3$ (Kanto Co.) were used as pore-formers for the β-LiAlO$_2$ agglomerates. The same composition of aqueous slurry (mole ratio of $LiO \cdot H_2O : \gamma\text{-}Al_2O_3 : NaOH = 7:1:8$) formulated by our research group was prepared [5] and different contents of pore-formers were used to reduce the time of washing and dispersion. The rod-shaped β-LiAlO$_2$ particles were crystallized by heat-treating the reaction mixture at 600 °C for 10 h. The heating rate was 5 °C/min. The final rod-shaped β-LiAlO$_2$ particles were obtained after removing NaOH, residual soluble components and not completely burnt-out additions by washing the reacted mixture with deionized water. In order to synthesis γ-LiAlO$_2$ particles, the rod-shaped β-LiAlO$_2$ particles were heat-treated in an alumina crucible at 750 °C for 3 h. This was necessary to in order complete the phase transformation of the β to the γ form.

The time of washing and dispersion of β-LiAlO$_2$ agglomerates was measured with a fixed amount of reaction mixture (116.2 g), but with different types and amounts of pore-formers, at room temperature. The crystalline phases and microstructures of the rod-shaped β-/γ-LiAlO$_2$ particles were analyzed by means of X-ray diffractometry (XRD; Model Rint 2700, Rigaku Co., Tokyo, Japan) and scanning electron microscopy (SEM; Model S4200, Hitachi, Ltd., Tokyo, Japan), respectively. The pore-size distribution was measured by mercury porosimetry (Model Autopore II, Micrometrics Instrument Corp., USA).

The reinforced matrices were fabricated by tape-casting, using rod-shaped γ-LiAlO$_2$ particles that were synthesized by the same method reported previously [7,8]. The performance of the reinforced matrices was measured by single-cell tests. The electrolyte layer consists of the non-reinforced matrix (hereafter, called standard matrix) and rod-shaped particle reinforced matrix filled with 62:38 mol% of $Li_2CO_3 : K_2CO_3$ mixture. Two single cells were prepared using standard matrices and rod-shaped particle reinforced matrices. Both cells were operated at 650 °C under atmospheric pressure. The fuel gases through the anode were 80% H_2 and 20% CO_2, both humidified at 50 °C, and the oxidant gases through cathode were 70% air and 30% CO_2. A thermal cycle test was carried out on the single cells (100 cm^2). After each of these tests, cell performance was evaluated. The cell voltages were measured at zero current (open-circuit voltage, OCV) and at 150 mA cm^{-2}, which is the normal load. The ohmic cell resistance was determined with a milliohm meter (Yokogawa Hewlett-Packard, HP-4776) at OCV. The gas composition at the anode exit was measured at OCV with a gas chromatograph (Hewlett-Packard 5890 series II, USA).

3. Results and discussion

3.1. Formation of pores

The primary role of pore-formers is to minimize the time required for washing and dispersion of β-LiAlO$_2$ agglomerates by making large pores in the reaction mixture. Furthermore, it is necessary that little ash and unexpected materials are produced during the whole process. Given these requirements, it was decided that carbon and ammonium carbonate were the most suitable pore-formers. In this work, the pore-formation process was based on the following reactions:

$$C + O_2 = CO_2 \tag{2}$$

$$(NH_4)_2CO_3 = 2NH_3 + CO_2 + H_2O \tag{3}$$
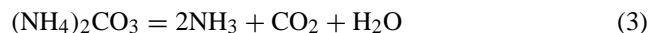
As described in reaction (2), carbon powders are gradually oxidized to CO_2 around 480 °C in an air atmosphere. They could not be sufficiently oxidized, however, due to the lack of oxygen in the reaction mixture. Therefore, in the case of carbon addition, it is important to minimize the formation of uncompleted reaction products or ashes by optimizing the amount of addition. Compared with reaction (2), it was found that ammonium carbonate (reaction (3)) is completely decomposed at temperatures below 100 °C.

3.2. Effect of pore-formers

The effect of pore-formers on the washing and dispersion of β-LiAlO$_2$ agglomerates was examined by SEM and mercury porosimetry. Morphological changes of β-LiAlO$_2$ agglomerates due to the addition of different types of pore-former in the reaction mixture are shown in Fig. 2. A large number of gaps are distributed among the rod-shaped particles. The gaps in Fig. 2(b) and especially in Fig. 2(c) are much wider in comparison with those in Fig. 2(a). As a
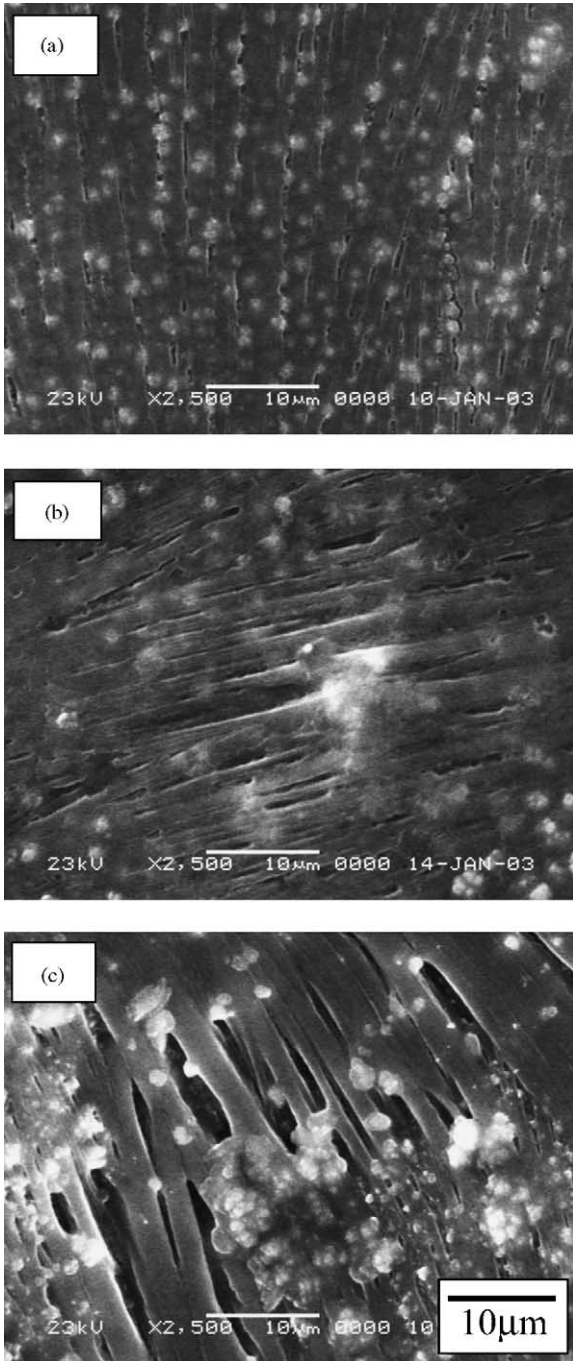
Fig. 2. Scanning electron micrographs of β-LiAlO₂ agglomerates synthesized from reaction mixtures with different types of pore-former: (a) no addition, (b) carbon 3 wt.%, (c) $(NH_4)_2CO_3$ 3 wt.%.

Fig. 3. Pore-size distributions of β-LiAlO₂ agglomerates with different types of pore-former.

quired to wash and disperse the β-LiAlO₂ agglomerates. Given this observation, a dispersibility test was performed. The dissociation time of the β-LiAlO₂ agglomerates with the change in the content of the respective pore-former is presented in Fig. 4. With carbon addition, the decrease in dissociation time is proportional to the amount of addition. When adding excess amounts of carbon powder (>5 wt.%), however, it is found that unexpected material (i.e., Li_2CO_3) and inadequately shaped β-/γ-LiAlO₂ particles appeared. Interestingly, ammonium carbonate addition shows a linear

Fig. 4. Time of washing and dispersion of β-LiAlO₂ agglomerates with deionized water in relation to amount of different type of pore-former.

numerical supplement to these phenomena, Fig. 3 shows the pore-size distributions of β-LiAlO₂ agglomerates according to the different types of pore-former. The average pore diameter of the β-LiAlO₂ agglomerates, in the case of adding carbon and ammonium carbonate, are estimated to be 80 and 100 μm, respectively. With no additions, the value is below 70 μm. By adding pore-formers, water can easily infiltrate through the large open pores and therefore less time is re-
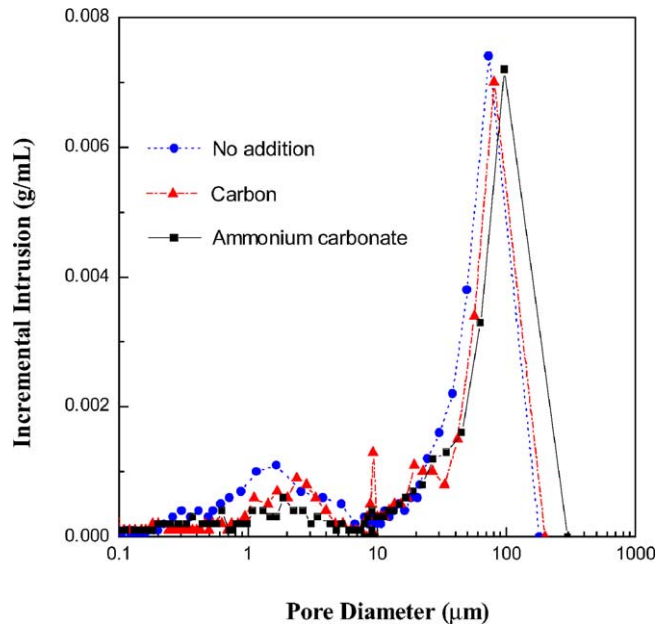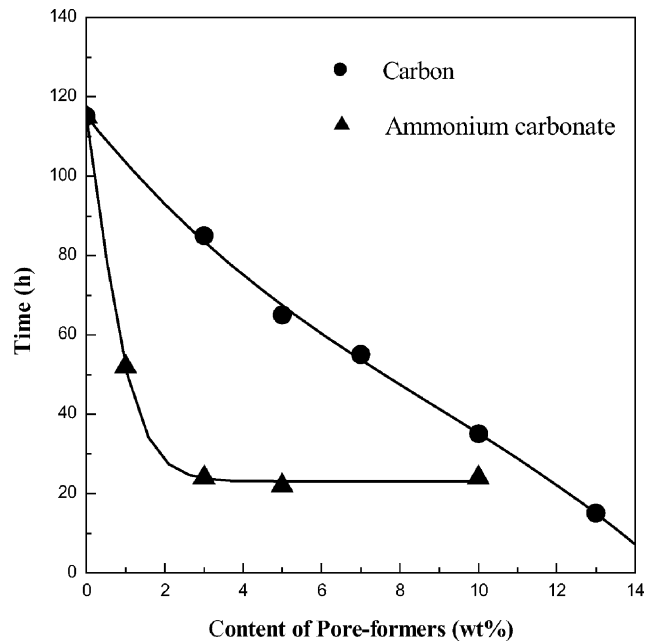
decrease of dissociation time in the range below 3 wt.%, while the dissociation time has a constant value of 20–30 h (average 25 h) after 3 wt.%. As a consequence, the reduction in washing and dispersion times is greater than for carbon. Accordingly, it is concluded that the optimum contents of carbon and ammonium carbonate in these studies are both 3 wt.%, but that ammonium carbonate is superior to carbon in terms of efficiency, handling, and the degree of purity.

3.3. Synthesis of rod-shaped β-/γ-LiAlO$_2$ particles

Given the above results, a fixed content (3 wt.%) of carbon and ammonium carbonate were utilized in the synthesis of β-/γ-LiAlO$_2$ particles. The morphological changes of these particles with different types of pore-former were observed by SEM (Fig. 5), and the crystalline phases were confirmed by X-ray analysis (Fig. 6). Most of the rod-shaped β-/γ-LiAlO$_2$ particles are 1 μm in diameter and 10–15 μm long (aspect ratios are 10–15) regardless of the type of pore-former. In addition, the crystal structures of rod-shaped γ-LiAlO$_2$ particles synthesized from the reaction mixture with pore-formers (see Fig. 6b–d) coincide exactly with that of commercial γ-LiAlO$_2$ powders (Fig. 6a). Thus, it can be concluded that the addition of pore-formers such as carbon or ammonium carbonate (<3 wt.%) does exert a negative influence on the synthesis of rod-shaped γ-LiAlO$_2$ particles via the transformation of rod-shaped β-LiAlO$_2$ particles.
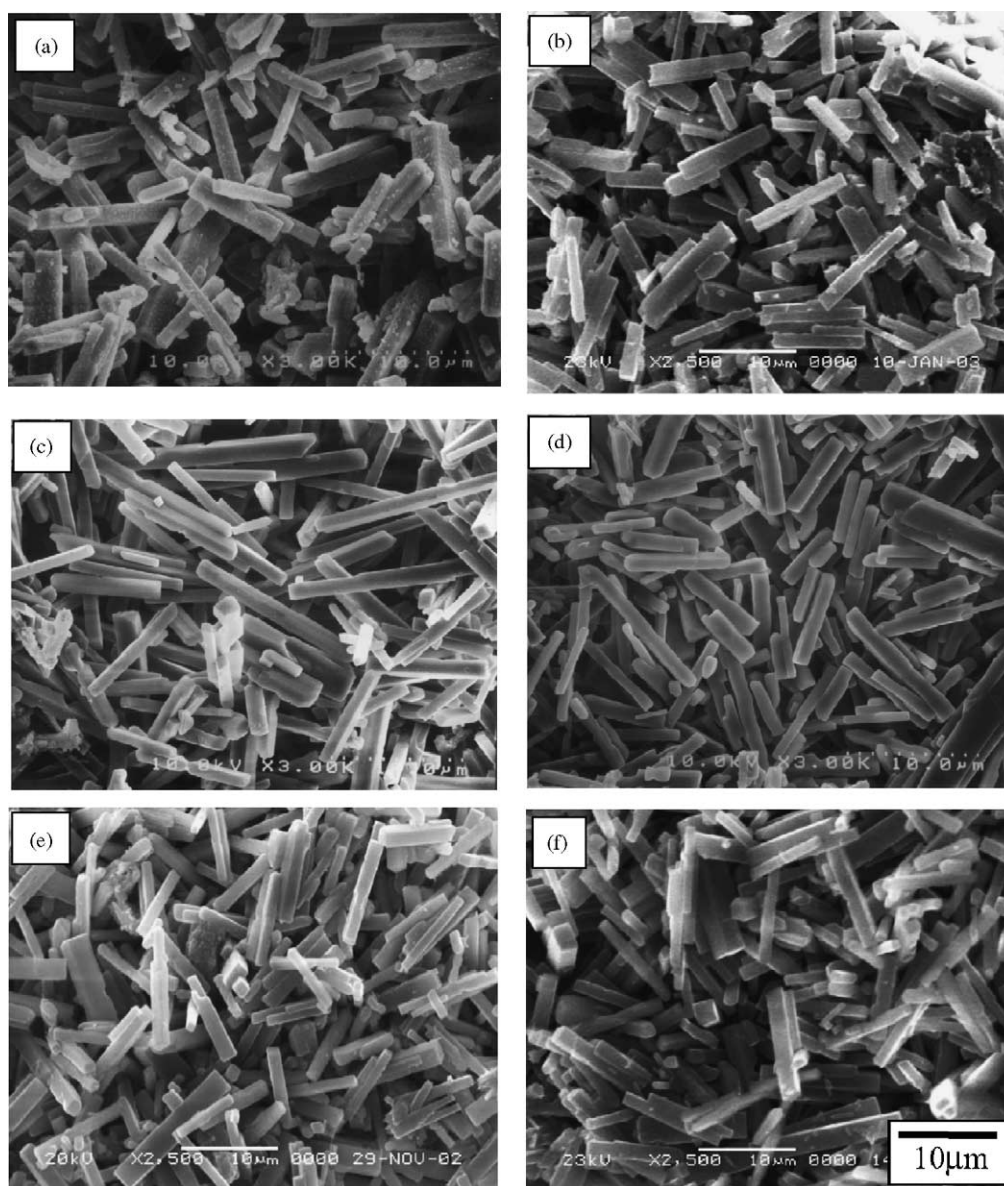

Fig. 5. Scanning electron micrographs of rod-shaped β-/γ-LiAlO$_2$ particles with different types of pore-former: (a) β-LiAlO$_2$ with no addition, (b) γ-LiAlO$_2$ with no addition, (c) β-LiAlO$_2$ with carbon addition, (d) γ-LiAlO$_2$ with carbon addition, (e) β-LiAlO$_2$ with (NH$_4$)$_2$CO$_3$ addition, (f) γ-LiAlO$_2$ with (NH$_4$)$_2$CO$_3$ addition.
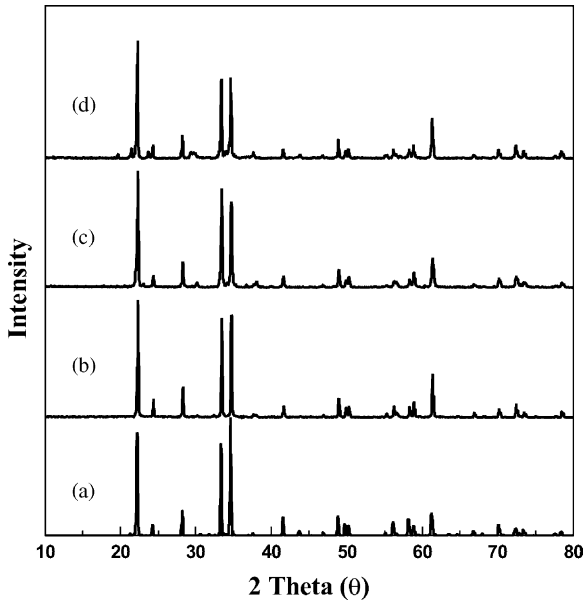
Fig. 6. XRD patterns of rod-shaped γ-LiAlO$_2$ particles with different types of pore-former: (a) commercial powder, (b) no addition, (c) carbon addition, (d) ammonium carbonate addition.

Moreover, the different types and amounts of addition are not a decisive factor in controlling the shape and aspect ratio of rod-shaped γ-LiAlO$_2$ particles.

3.4. Performance of matrics reinforced with rod-shaped particles

The occurrence of cracks in the matrices can be determined by measuring the amount of gas cross-over. Since N$_2$ gas is a cathode oxidant gas, measurement at this gas at the anode exit can determine the occurrence of gas cross-over. The N$_2$ gas composition in the anode exit gas is given in
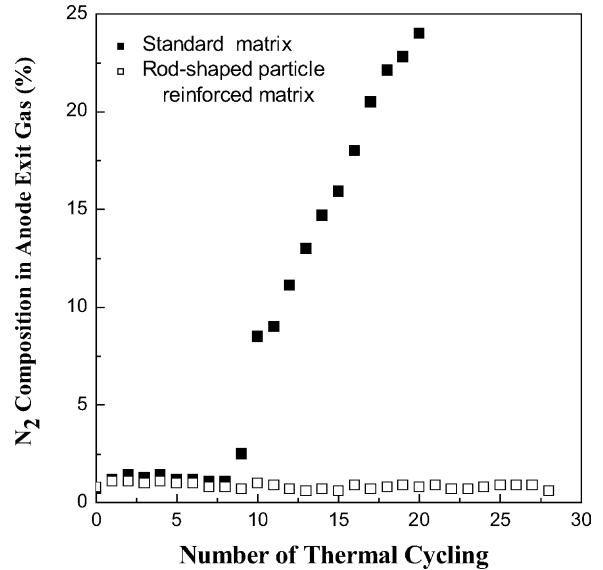

Fig. 7. N$_2$ cross-over in single cells due to thermal cycling.

Fig. 7. For standard matrices, N$_2$ gas cross-over is under 3%, which is the general default range, during the first nine thermal cycles. N$_2$ gas cross-over increases appreciably, however, after the tenth thermal cycle (8.5%). This observation suggests a high occurrence of cracks in the matrices. It is found the incidence of such cracks increases severely after the twentieth thermal cycle, in which N$_2$ gas cross-over is 22.8%. On the other hand, in the cell using rod-shaped particle reinforced matrices, N$_2$ crossover remains below 3% during 28 thermal cycles, consequently, such reinforced matrices have superior thermal stability to that of a standard matrix.

The occurrence of cracks in the matrices can also be evaluated by measuring the OCV of a single cell. The variation
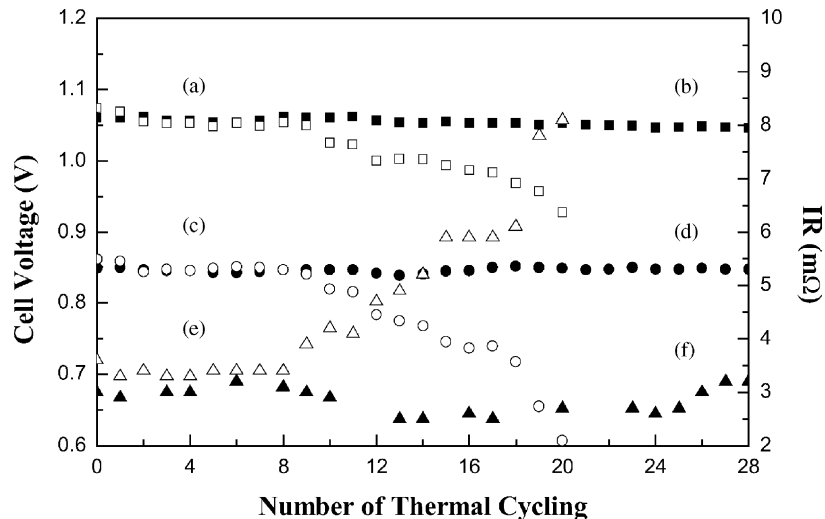

Fig. 8. Cell performance: (a) OCV of standard γ-LiAlO$_2$ matrix (□); (b) OCV of rod-shaped particle reinforced matrix (■); (c) cell voltage (150 mA cm^{-2}) of standard γ-LiAlO$_2$ matrix (○); (d) cell voltage (150 mA cm^{-2}) of rod-shaped particle reinforced matrix (●); (e) internal resistance of standard γ-LiAlO$_2$ matrix (△); (f) internal resistance of rod-shaped particle reinforced matrix (▲).

in cell performance due to thermal cycles is shown in Fig. 8. For a single-cell with a standard matrix, the OCV is 1.050 V and the initial cell voltage at $150\,\mathrm{mA\,cm^{-2}}$ is 0.87 V. After 10 cycles, during which the N_2 gas cross-over is significantly increase, the OCV has decrease to 1.025V. Thereafter, the OCV decreases gradually and becomes 0.928 V after 20 cycles. The cell voltage at $150\,\mathrm{mA\,cm^{-2}}$ exhibits a similar trend. On the other hand, in the case of rod-shaped particle reinforced matrices, the OCV is 1.060 V and the initial cell voltage at $150\,\mathrm{mA\,cm^{-2}}$ is 0.849 V. The OCV remains at approximately 1.047 V while the cell voltage at $150\,\mathrm{mA\,cm^{-2}}$ is over 0.840 V during all 28 thermal cycles. This confirms that cell performance using rod-shaped particle reinforced matrices is greatly improved in comparison with non-reinforced standard matrices.

4. Conclusions

An effective fabrication of rod-shaped γ-LiAlO$_2$ particles for the reinforcement of MCFC matrices has been successfully achieve via synthesis of porous β-LiAlO$_2$ agglomerates by adding pore-formers to the reaction mixtures. The main findings of this research are as follows:

1. The addition of carbon (YP-17) and ammonium carbonate effectively reduce the time of synthesizing rod-shaped γ-LiAlO$_2$ particles without introducing any residual products. With excess amounts of carbon powders (>5 wt.%), however, it unexpected material (i.e., Li_2CO_3) and inadequately shaped β-/γ-LiAlO$_2$ particles appear.
2. Regardless of the type of pore-former, most of the rod-shaped β-/γ-LiAlO$_2$ particles produced are $1\,\mu m$

in diameter and 10–$15\,\mu m$ in length (aspect ratios $= 10$–15).
3. The crystal structure of rod-shaped γ-LiAlO$_2$ particles synthesized from the reaction mixture with pore-formers coincides exactly with that of commercial γ-LiAlO$_2$ powders.
4. There is an appreciable improvement in cell performance using rod-shaped particles reinforced matrices.

Acknowledgements

References

[1] S. Terada, I. Nagashima, K. Higaki, Y. Ito, J. Power Sources 75 (1998) 223–229.
[2] A.J. Appleby, F.R. Foulkes, Fuel Cell Handbook, Van Nostrand Reinhold, New York, 1989, pp. 557–558.
[3] J.Y. Cho, S.H. Hyun, S.A. Hong, J. Am. Ceram. Sci. 84 (5) (2001) 937–940.
[4] K. Takizawa, A. Hagiwara, J. Power Sources 109 (2002) 127–135.
[5] S.H. Hyun, S.C. Cho, J.Y. Cho, D.H. Ko, S.A. Hong, J. Mater. Sci. 36 (2001) 441–450.
[6] K. Suzuki, T. Kakihara, Y. Yamamasu, T. Sasa, Mater. Res. Soc. Symp. Proc. 371 (1995) 297.
[7] G. Saeki, H. Takahashi, A. Watanabe, J. Ceram. Soc. Jpn. 104 (3) (1996) 221.
[8] S.H. Hyun, G.H. Beak, S.A. Hong, J. Korean Ceram. Soc. 34 (3) (1997) 303–313.
[9] S.H. Hyun, S.C. Cho, S.A. Hong, J. Korean Ceram. Soc. 36 (2) (1999) 107–115.