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Mechanical properties of the lithium aluminate matrix for MCFC reinforced with metal oxide materials

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ABSTRACT

In this study, the electrolyte matrix was reinforced by metal wire mesh which has a thickness in the range of 0.30–0.33 mm. Both pure $LiAlO_2$ matrix green sheet and the matrix reinforced by metal mesh were prepared by tape casting and hot pressing methods, respectively. Mechanical properties and resistance against cracking of each matrix samples were investigated in 650 °C by differential pressure and single cell test. When applying both differential pressure and single cell test in the reinforced matrix, N_2 cross-over percentage was maintained in 0.1–0.9% constantly. In conclusion, metal wire mesh is a good additive to increase mechanical strength and durability of ceramic composites.

1. Introduction

The molten carbonate fuel cell is one of the most attractive types of fuel cells and has the potential to replace conventional thermal power plants, and their development is progressing to such an extent that some prototype demonstration power plant tests have already experienced. Although the effort directed at their technical realization is substantial, optimized resolution in ensuring sufficient durability for such fuel cells still remains as a significant technical issue. The electrolyte matrix of MCFC is used for electronic insulation and ionic communication between electrodes. However due to poor mechanical strength of ceramic materials, the problem of the crack in $LiAlO_2$ matrix for MCFC appeared when the cells are stacked and operated at high temperature has prompted interested in development of reinforced matrix which has high mechanical properties.

To increase the mechanical strength of the matrix including resistance against cracking and long term durability, the matrix was reinforced with metal wire mesh which is stronger in bending strength and more economical than any other additives for reinforcement like large metal particle and fiber [1]. Resistance against cracking and durability were investigated by differential pressure and standard single cell test.

2. Experiments

The pure matrix green sheet was fabricated by tape casting of the slurry which is consisted of dispersant, binder, plasticizer, defoamer, organic solvent and raw powder of commercial $LiAlO_2$ particles (Chemetall Foote Co.) which have 1 μm particle size.

DisperBYK-110 (BYK Chemie Co.) was used as dispersant, polyvinyl butyral (Solutia Co.) as binder, dibutyl phthalate (Junsei chemical Co.) as plasticizer, SN D-348 (San Nopco, Korea) as defoamer and mixture of toluene (99.5%, Daejung Co.) and ethyl alcohol anhydrous (99.0%, Daejung Co.) in the weight ratio 7:3 as solvent. The slurry composition is shown in Table 1. The constituents were mixed for 96 h by ball milling process.

The matrix reinforced by metal wire mesh was fabricated from pure $LiAlO_2$ green sheets by hot pressing method. In this study, stainless steel-40 (AISI type No. 304) mesh which has a diameter in the range of 0.30–0.33 mm was used as metal wire mesh. The conditions of the hot pressing method were given in Table 2. To observe pore structure of matrix, each matrix green sheet which was heat-treated at 650 °C for 5 h was analyzed by environmental scanning electronic microscopy (ESEM, FEI XL-30 FEG) and mercury porosimetry (Autopore II, Micrometrics Instrument Co.).

Differential pressure test for evaluating mechanical strength of the matrix was carried out in the same condition of conventional single cell test except that it was not included electrodes in the modified cell frames. In this test, both N_2 cross-over percentage and cathode output gas flow rate were investigated. Moreover, the single cell (10 cm × 10 cm) test was used to evaluate durability for long term operation. In the single cell test, not only N_2

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Table 1
The slurry composition of the pure $LiAlO_2$ matrix.

Material		wt.%
Raw powder ($LiAlO_2$)		36.298
Dispersant (DisperBYK-110)		1.089
Binder (polyvinyl butyral)		9.074
Plasticizer (dibutyl phthalate)		5.808
Defoamer (SN D-348)		0.544
Solvent	Toluene	33.031
	Ethanol	14.156

Table 2
The conditions of the hot pressing method.

Pressure (kg_f/cm^2)	Temperature (°C)	Time (min)
30	50	30

cross-over and cathode flow but also cell performance were measured by gas chromatography (Hewlett–Packard 5890 series II, USA) and digital bubble flow meter (Agilent Optiflow 650), respectively.

3. Results and discussion

ESEM image of pure $LiAlO_2$ matrix showed that the particles make uniform pore structure with bonding among each other. The mesh-matrix interfaces enable to promote crack deflection and frictional sliding [2]. Closed mesh-matrix interfaces were observed in the ESEM image of reinforced matrix. However, there were some gaps around the interface due to fabrication problems (Fig. 1).

To hold the electrolyte stably in the cell, the pore size of the matrix must be smaller than that of electrodes, considering capillary force. Furthermore, the change of porosity and pore size distribution between pure matrix and mesh-reinforced matrix should not occur. Conventionally, matrix for MCFC requires high porosity (50–70%) and a sharp pore size distribution (0.1–0.3 μm) [3]. As shown in Fig. 2, when the mesh matrix was fabricated from pure matrix by hot pressing method, porosity and medium pore size were changed from 56.05% to 52.86% and from 0.24 to 0.26 μm, respectively. It was considered that possession of the non-porous metal mesh caused the decrease of porosity and some gaps around the interface led to increase the pore size. However, the change in porosity and pore size of the mesh matrix were considered negligible to the test.

Differential pressure test was conducted for evaluating the mechanical strength of active part which was estimated by N_2 cross-over percentage and wet sealing part estimated by cathode output gas flow rate when needle valve was closed gradually. In the active area where reaction gas flows constantly, each cell had almost the same level of N_2 cross-over percentage in the range 0.07–0.15%. But in the wet sealing area, remarkable difference of decrease rate of cathode output gas flow between pure matrix and mesh-matrix cell occurred.

The metallic parts (current collectors and wet sealing material) in MCFC systems often suffer from hot corrosion where the oxide layer is attacked by molten salt, dissolved and re-precipitated again, causing a porous non-protective oxide layer that do not hinder further attacks on the material. Moreover, the corrosion processes often cause a permanent loss of electrolyte by forming corrosion products containing lithium or potassium [4]. The corrosion can cause over 20% of the total electrolyte loss during operation [5].

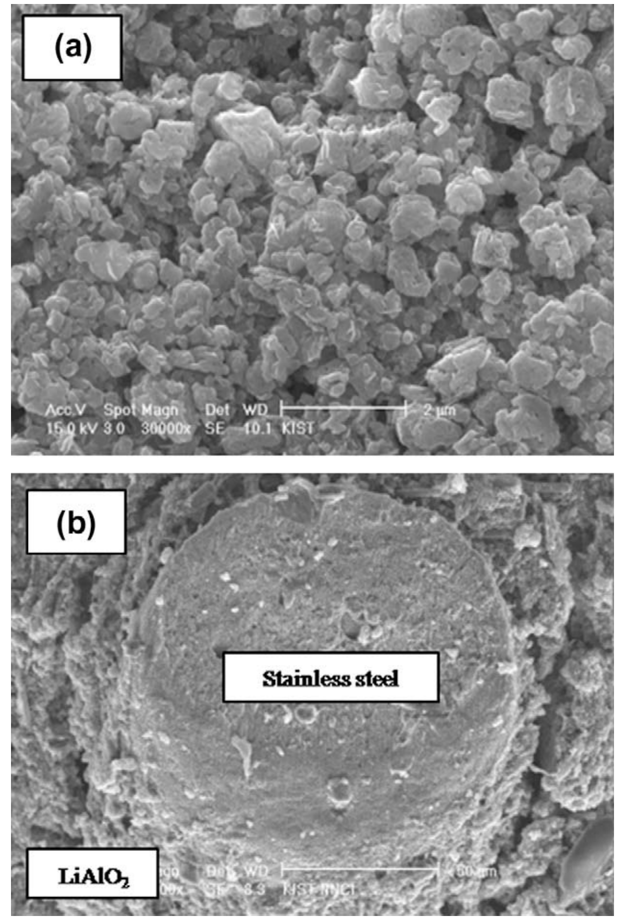

Fig. 1. ESEM image of (a) pure matrix and (b) mesh matrix.

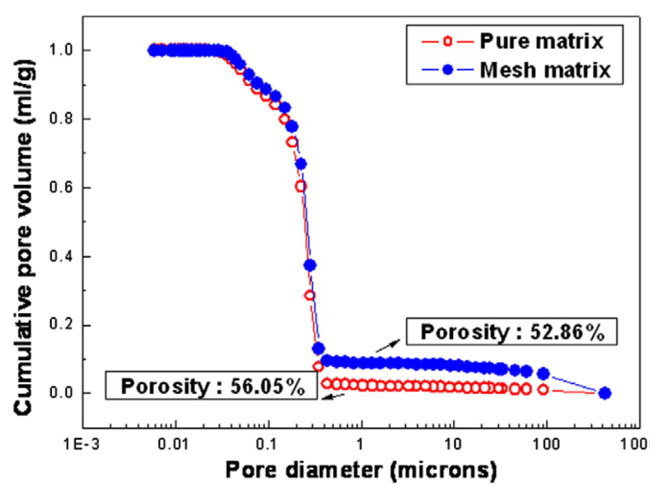

Fig. 2. Pore size distribution of pure and mesh matrix.

In this case, it was considered that the difference of mechanical strength occurred in wet sealing part which contains less electrolyte due to hot corrosion.

When increasing differential pressure from 0 to 0.6 bar gradually, the flow decrease rate of the pure matrix and mesh matrix was 77.5 ccm/0.1 bar and 21.7 ccm/0.1 bar, respectively, while N_2 cross-over of each cell was maintained in 0.07–0.15% constantly as shown in Figs. 3 and 4. In other words, the mechanical strength was improved about three times by adding metal wire mesh.