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Using aluminum and Li_2CO_3 particles to reinforce the α-$LiAlO_2$ matrix for molten carbonate fuel cells

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ABSTRACT

The electrolyte substrate (matrix) of a molten carbonate fuel cell (MCFC) provides both ionic conduction and gas sealing. During the starting-up and operating of MCFC stacks at 923 K, the matrix can experience mechanical stresses that can cause cracking. In particular, the pure α-$LiAlO_2$ that is generally used for the MCFC possesses poor mechanical strength. In this study, we employed Al and Li_2CO_3 particles as reinforcement materials to increase the mechanical strength of the α-$LiAlO_2$ matrix for its stable long-term operation. The mechanical strength of the matrix increased dramatically after adding Al particles into the pure matrix. Moreover, we operated a single cell for 2000 h after adding Li_2CO_3 particles into the Al-reinforced matrix to prevent a Li-ion shortage caused by a lithiated Al reaction in the matrix.

1. Introduction

Molten carbonate fuel cells (MCFCs), which are usually operated at 923 K, have great potential as replacements for conventional thermal power plants; their development is progressing to such an extent that some prototype demonstration power plant tests have already been performed [1,2]. MCFCs possess several advantageous properties, including high efficiency, fuel flexibility, and cogeneration capability [3,4], relative to low-temperature fuel cells. The commercialization of MCFCs, however, will require some technical problems to be solved, especially, the development of long-life cell components, because the volatile and highly corrosive carbonate melt restricts the cell life-time [5].

Among the components for MCFC, the matrix plays an important role in supporting the electrolyte. Therefore, it should have an appropriate pore structure and mechanical strength to provide effective gas-sealing properties without cracks forming in the matrix during MCFC operation. Various approaches for improving the crack resistance and extending the life of the electrolyte matrix have been proposed. A composite of $LiAlO_2$ and alumina fiber has been developed to improve the mechanical strength of the matrix [6], but it is not easy to commercialize because of its high cost [7], and the

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fact that alumina fibers decay gradually in molten carbonates at the MCFC operating temperature [8]. Aluminum (Al) particles are attractive and alternative reinforcement additives because of their good sintering ability and low cost. Recently, γ-$LiAlO_2$ was found to undergo particle growth, and the crystal phase of the $LiAlO_2$ in the MCFC matrix was transformed from γ- to α-$LiAlO_2$, during operation of a MCFC [9–11]. In addition, Ostwald ripening was found to transform smaller particles into large particles through diffusion and the particle growth [12]. Tomimatsu et al. [13] observed, however, that the α-$LiAlO_2$ particles did not grow appreciably after more than 7550 h in the electrolyte at high temperature. As a result of these studies, α-$LiAlO_2$ has become the matrix material of choice despite its low mechanical strength [10].

In this study, we used α-$LiAlO_2$ as the matrix and both Al and Li_2CO_3 particles as reinforcement material to develop a matrix that would be stable for long-term operation and exhibit increased mechanical strength.

2. Experimental

2.1. Fabrication of matrix

The matrix for the MCFC was fabricated through tape casting of a slurry comprising a dispersant (DisperBYK-110, BYK Chemie Co.), binder (polyvinyl butyral, Solutia Co.), plasticizer (dibutyl phthalate, Junsei chemical Co.), defoamer (SN D-348, San Nopco, Korea), organic solvent [a 7:3 (w/w) mixture of toluene (99.5%, Deajung Co.) and anhydrous ethyl alcohol (99.0%, Deajung Co.)], and raw powders of commercial α-$LiAlO_2$ (Chemetall Foote Co.; particle diameter: 2 μm) and Al (High Purity Chemical Co.; particle diameter: 3 or 30 μm). These components were mixed for 4 days through the first and second ball milling processes. Tape casting was then performed to obtain green sheets. The amount of reinforcing-aid material in the matrix slurry was fixed at 10 or 30 wt% based on the weight of raw power (α-$LiAlO_2$) and each matrix green sheet was made in the thickness of 0.3 mm. A flow chart for the overall experiment is presented in Fig. 1; the slurry composition is listed in Table 1.

2.2. Microstructure and mechanical strength

Each matrix green sheet was burned-out at 923 K for 10 h to eliminate the organic components; it was then characterized using out-of-cell tests, such as bending strength tests, and analyses of pore sizes, and porosity. Scanning electronic microscopy (ESEM, FEI XL-30 FEG) and mercury porosimetry (Autopore II, Micrometrics Instrument Co.) were used to observe the microstructure of each matrix. Three-point bending strength tests were performed using a bending test machine (QC-508E, Cometech Co.) to investigate the mechanical strength of each burned-out matrix which has the thickness of 0.3 mm.

2.3. Crossover tests

Two types of test were performed; differential pressure and protrusion tests were conducted under the same conditions as summarized in Table 2. The fuel gas that passed through the anode was a mixture of H_2, CO_2, and H_2O in a 72:18:10 mole ratio; the cathode gas was air and CO_2 in a 70:30 ratio. All matrix used in these tests consist of four green sheets which have the thickness of 0.3 mm. Therefore, the total thickness of the matrix in each single cell was 1.2 mm. The presence of cracks in the matrix was investigated in three ways; the N_2 crossover, measured by gas chromatography (Hewlett-Packard 5890 series II, USA), in the anode exit for the cathode oxidant gas that flowed through leaks in the matrix; the cathode output flow rate, measured using digital bubble flow meter (Agilent Optiflow 650), in the cathode exit; and assessment of the open-circuit voltage (OCV).

The differential pressure test for evaluating crack formation in the matrix, by applying differential pressure between the anode and cathode gas flow channels, was performed using a needle valve located in the cathode output gas flow channel. Each differential pressure test was evaluated by measuring the N_2 crossover amount, the cathode output flow

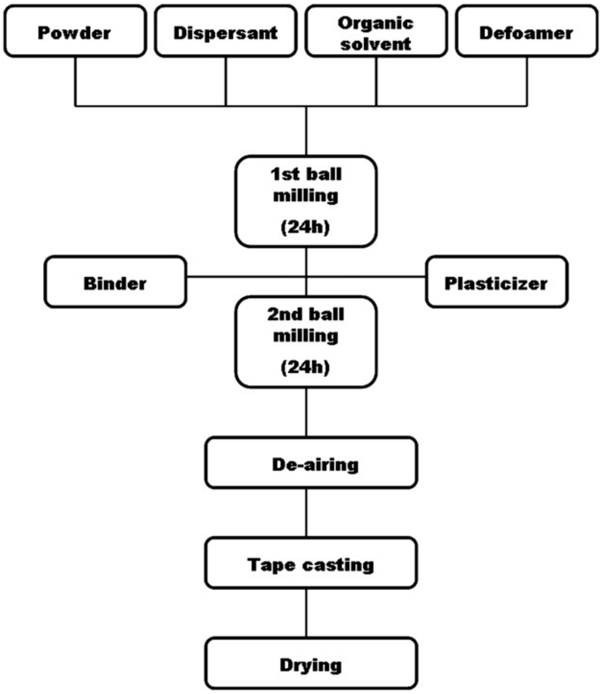

Fig. 1 – Overall process flow chart.

Table 1 – Slurry compositions of the pure and Al-reinforced matrices.

Material		wt.%
Raw powder		36.3
Dispersant (DisperBYK-110)		1.1
Binder (Polyvinyl butyral)		9.1
Plasticizer (Dibutyl phthalate)		5.8
Defoamer (SN D-348)		0.5
Solvent	Toluene	33.0
	Ethanol	14.2