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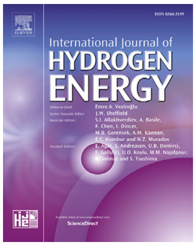

Manufacturing of γ-$LiAlO_2$ matrix for molten carbonate fuel cell by high-energy milling

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ABSTRACT

Molten carbonate fuel cells (MCFCs) are promising high temperature power generating devices. However, unlike solid oxide fuel cells (SOFCs) they utilize a liquid electrolyte which must be immobilized in a porous matrix.

In this paper, a slurry composition for lithium aluminate (γ-$LiAlO_2$) matrix was developed and green matrices were subsequently formed by the tape casting method. In order to achieve the desired structure of the matrix (pore size, porosity) γ-$LiAlO_2$ powder was milled in a planetary ball mill for 18 h with a solvent, dispersant and defoamer. After this step, other ingredients were added, including a binder and plasticizer to obtain optimal rheology of the slurry. Cell tests confirmed optimal performance of the matrix compared to the third party reference γ-$LiAlO_2$ matrices. Burned out matrix was characterized by scanning electron microscopy (SEM) and laser diffraction in order to determine the γ-$LiAlO_2$ powder particle size and morphology. The results show that high-energy milling enabled a fine pore structure and high specific surface area of the matrix to be obtained in a relatively short time, compared to conventional fabrication routes. The matrix structure obtained within this study is suitable for high performance operation of MCFC.

Introduction

Molten carbonate fuel fells (MCFCs) are amongst the most efficient power generating devices available [1]. Compared to low temperature fuel cells, they are more flexible in terms of fueling and do not need precious or rare earth metal catalysts, as low cost nickel exhibits strong catalytic activity at the high working temperature of the cell [2,3]. In addition, CO and CH_4 can be internally converted on the Ni anode of MCFC whereas – in low-temperature fuel cells – platinum catalysts are poisoned by the presence of CO.

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MCFCs use a molten electrolyte consisting of lithium/potassium/sodium carbonates, where the eutectic mixtures of Li/K and Li/Na are most commonly used [4]. The liquid electrolyte must be held between electrodes by a porous, inert matrix which enjoys high electrical resistivity and does not deteriorate in the corrosive environment.

Electrolyte matrix is most commonly produced from lithium aluminate (γ-$LiAlO_2$) by tape casting a ceramic/polymer slurry prepared by the time consuming ball-milling process, during which the base material undergoes refinement [5,6]. The γ-$LiAlO_2$ powder is typically embedded in a PVB polymer binder, which is burned out during the start-up procedure (PVB decomposes at around 400 °C [7]). This leaves the porous structure to be filled with electrolyte melt. Infiltration of the matrix by the electrolyte is based on capillary action, which requires good wettability of the material and a fine pore structure, with pore size in the range of single micrometers. Due to that, the matrix gets completely filled with the electrolyte melt, having the smallest pores in the component stack [8].

Penetrating pressure (between the anode and the cathode) corresponds to pore radius – r – in the matrix, which can be calculated from the Young-Laplace equation:

$$P = \frac{2\delta\cos\theta}{r} \tag{1}$$

δ – coefficient of surface tension of the electrolyte, is $\delta = 0.198\ \mathrm{N\,m^{-1}}$ and θ – contact angle between the matrix and electrolyte, is $\theta = 0°$ [9].

Assuming a pressure difference of 10^5 Pa [10], the pore radius must be 3.96 μm. If the pore size is reduced, the electrolyte matrix can withstand a greater pressure difference without gas crossover occurring, thus powder grain size must be controlled to ensure adequate capillary action. However, the impact of particle size and specific surface area of the matrix on cell performance has not been reported in the past.

In addition to controlling the pore structure of the matrix, it is essential to avoid the matrix cracking during the start-up and operation of the molten carbonate fuel cell. Accordingly, great efforts have been put into increasing its mechanical strength. Existing research papers regarding reinforcement of a lithium aluminate matrix report the addition of aluminum and Li_2CO_3 particles to the α-$LiAlO_2$ matrix [1,11], using a stainless steel wire mesh (approx. 0.3 mm thick) [12] and aluminum foam [13]. A noteworthy, novel approach to green tape fabrication was presented in Ref. [14], where powder extrusion was employed.

In this work, high energy planetary ball milling was used to produce the required refined hard ceramic base powder. This method gives a controllable degree of refinement by adjusting the milling speed, amount and size of grinding media (ball diameter), and milling time. Planetary milling was successfully utilized to refine the particle size of the γ-$LiAlO_2$ for the MCFC matrix during slurry preparation. The manufactured matrix was characterized by scanning electron microscopy (SEM) and laser diffraction. The fine pore structure and high specific surface area of the matrix were deemed suitable for high performance operation.

Experimental procedure

Matrix fabrication

The matrix was manufactured by tape casting ceramic/polymer slurry. The tape caster used for this task was a moving-blade device, and the doctor blade height was set to 0.55 mm. This technique was chosen for its repeatable results, scalability and quick turnaround.

The base ceramic material – raw γ-$LiAlO_2$ powder (ABCR GmbH) – was subject to laser scattering particle size analysis (Horiba LA-950) in order to determine the particle size distribution of the powder, as shown in Fig. 1.

The slurry was prepared by planetary ball milling in order to reduce the particle size of the γ-$LiAlO_2$ powder, thus leading to smaller pore size of the matrix, as required for proper operation of the cell (e.g. gas leak prevention) [9]. Moreover, this technique enables uniform slurry to be obtained without powder/binder agglomerates. $LiAlO_2$ powder was milled in sintered zirconia containers with 5 mm zirconia balls in Retsch PM400 mill at 250 rpm for 18 h.

The first milling was conducted with ethanol (Avantor Performance Materials Poland), Solsperse 20000 dispersant (Lubrizol Advanced Materials) and Agitan DF300 M defoamer (Munzing Chemie GmbH). This composition led to successful milling, due to low viscosity and good dispersion of the powder. After this step, other ingredients were added including: Mowital B60H PVB binder (Kuraray America) and dibutyl phthalate (DBP) plasticizer (Aktyn). The complete slurry composition was subsequently milled for an additional 3 h and vacuum de-aired (0.1 bar, 30 s) to obtain homogeneous slurry for tape casting. A flowchart of these steps is presented in Fig. 2.

Characterization and testing

In order to investigate the structure of the matrix with scanning electron microscopy, green tapes were heated slowly to

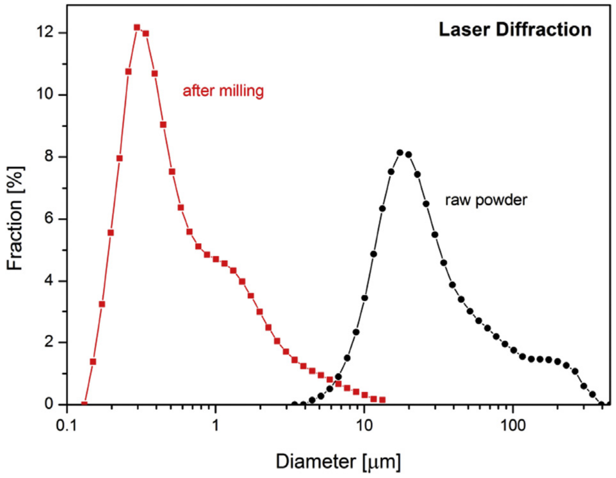

Fig. 1 – Particle size distribution of base γ-$LiAlO_2$ powder (Horiba LA-950 analyzer) shows that raw powder is too coarse for capillary retention of electrolyte. Planetary ball milled powder (after 18 h) has a mean size of under 0.5 μm.