

Research Article

The Optimization of Matrix Preparation Process and Performance Testing for Molten Carbonate Fuel Cell

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A key component in the molten carbonate fuel cell (MCFC) is electrolyte matrix, which provides both ionic conduction and gas sealing. The aim of this work is to investigate the effects of selected operating conditions on the performance of the matrix preparation. Slurries were prepared to produce matrices by the technique of tape casting. The characteristics of the slurries and matrices were examined by laser particle size analyzer, scanning electron microscopy, and BET surface area analyzer. The testing results revealed that a slurry composition with 40 wt.% lithium aluminate was the optimal formulation to produce a good matrix with a pore size distribution of 0.1–0.4 μm and porosity of 50 vol.%. Coarse and fine LiAlO_2 particles were added in the matrix slurry to enhance the mechanical strength. Several green sheets were heated and pressed to enhance the bulk density to get a dense matrix of MCFC. Finally, a single MCFC was assembled and tested. The testing results showed the matrix with 40% solid loading gave the maximum discharge current of 20 A at 0.56 V.

1. Introduction

The electrolyte matrix is a key component in MCFC [1], which provides both ionic conduction and gas sealing. LiAlO_2 powder is typically used as material for electrolyte matrices. The matrix in MCFC must fulfill certain conditions such as (1) free crack, free big pore, and good mechanical strength; (2) being full of molten carbonate and perfect for keeping the carbonate [2]; (3) good ionic conductivity; (4) porosity in the range of 40–70% [3].

MCFC matrices are usually fabricated by tape casting. Slurry preparation is the most critical step in matrix tape casting. LiAlO_2 powder, organic binder, plasticizer, dispersant, and other additives are added into a kind of solvent and mixed with a ball mill to obtain uniform and stable slurry with certain fluidity. The selection of LiAlO_2 powder particle size, solvent, dispersant, binder, and plasticizer is very important to the process of tape casting and directly affects the performance of tape casting slurry, thus the performance of green sheets, and eventually the performance of hot-pressed matrices. Lee et al. [1] studied the Al reinforced matrix to improve its thermal stability. Batra et al. [4]

prepared an alpha lithium aluminate matrix and described the characteristics of the matrix. The current development efforts focus mainly on optimizing the matrix structure and performance. So far, no systematic analysis related to the good matrix preparation process was made.

In order to investigate the effects of preparation conditions on the performance of electrolyte matrix, in this study, ceramic slurries with different weight ratios of LiAlO_2 solid loading to the organic compounds were prepared to produce matrices with the technique of tape casting. The characteristics of the slurries and matrices were examined by laser particle size analyzer (S3500, Microtrac, USA), scanning electron microscopy (JSM-6010LV, JEOL, Japan), and BET surface area analyzer (ASAP 2020, Micromeritics, USA). An optimal matrix was prepared, and its performance was tested on gas crossover in the matrix and by discharge of MCFC under its operating conditions.

2. Experimental Method

2.1. Matrix Fabrication. The $\alpha\text{-LiAlO}_2$ and $\gamma\text{-LiAlO}_2$ (1:1 molar ratio) [5] powders were used as the solid constituent

TABLE 1: Tape casting slurry composition of the matrix (wt. %).

Sample name	Solid	Solvent	Binder	Plasticizer	Dispersant	Defoamer	Al ₂ O ₃ fiber
a	25	59	8	6	1.2	0.6	0.2
b	30	52	9	7	1.2	0.6	0.2
c	35	43	12	8	1.3	0.6	0.1
d	40	36	13	9	1.3	0.6	0.1

of MCFC matrix. The α -LiAlO₂ and γ -LiAlO₂ powders were made from boehmite reacting with Li₂CO₃ and LiOH, respectively. The mixture of cyclohexanone and butyl alcohol (1:1 volume ratio) was used as the organic solvent. Polyvinylbutyral (PVB) was used as a binder. In the additives, polyethylene glycol was used as a plasticizer, triolein as a dispersant, silicone oil as a defoamer, and Al₂O₃ fiber as reinforced material. The slurry composition is given in Table 1.

The ratio of binder, solvent, plasticizer, dispersant, and LiAlO₂ powder in the slurry was varied to obtain LiAlO₂ powder loading in the range of 25–40 wt.%. The slurry was prepared by ball milling of LiAlO₂ powder for 10 h at speed of 350 rpm in the solvent which contained the dispersant. Then the binder (PVB) and plasticizer were put into the mixture and ball mill for 5 h. Subsequently defoamer and Al₂O₃ fiber were added into ball milling for another 2 h. The slurry was filtered and vacuumed to remove bubbles. Green sheet of 10 cm × 10 cm dimension was prepared by tape casting on a smooth glass surface. To obtain a good matrix for cell testing, 3–5 pieces of green sheet were heated at 80°C and pressed, 3–5 pieces of green sheet were heated at 80°C and pressed to form one matrix under the pressure of 6 MPa. A flow chart [6] of the overall matrix preparation processes was presented in Figure 1.

2.2. Characterization. A laser particle size analyzer was used to measure the LiAlO₂ particulate size distribution in different kinds of slurries mentioned above. Scanning electron microscopy was employed to study the morphology of the green sheet. BET surface area analyzer was used to examine the porosity and the pore size distribution of matrix after organic ingredients burned out.

2.3. Matrix Performance Testing. To evaluate the matrix performance for gas sealing, a single MCFC was assembled. Testing was conducted with an 11 cm × 11 cm cell which had an electrochemical active area of 10 cm × 10 cm [4]. The anode and cathode were made of nickel carbonyl and prepared by the technique of pasting slurry. They had typical porosity of 60 vol.%–70 vol.% and pore size in range of 5–10 μ m [7]. The matrix was prepared by several green sheets, which were produced with the slurry of 40 wt.% LiAlO₂ powder loading. The carbonate electrolyte was prepared by Li₂CO₃ and K₂CO₃ with molar ratio of 62 to 38 [8]. The optimal matrix and two carbonate green sheets were stacked as a sandwich. Stainless steel end plates and the matrix with the carbonate sheets were assembled into a single cell. The matrix and the electrolyte sheets were in situ sintered. The performance of

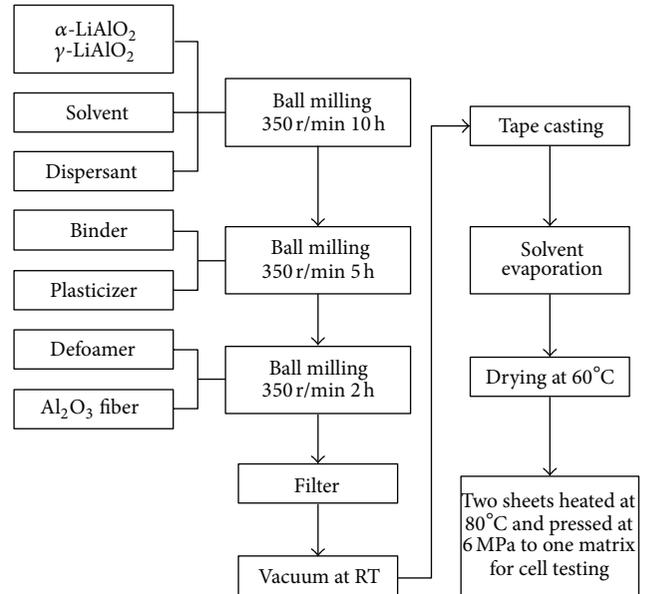


FIGURE 1: Flow chart of overall matrix preparation processes.

the unit cell was tested with SUN-FEL10A electronic load (Dalian Sunrise Power Limited-Liability Company).

3. Results and Discussion

3.1. Slurry Characterization. The matrix is an important component in MCFC; every aspect of its production could influence the final performance of the cell. The pore size distribution of the matrix was determined by the particle size of LiAlO₂ and the organic ingredients in the slurry. According to the Yong-Laplace equation [3]

$$P = \frac{2\delta \cos \theta}{r} \quad (1)$$

δ , coefficient of surface tension of the electrolyte, is 0.198 NM⁻¹ and θ , contact angle between the matrix and the electrolyte, is $\theta = 0^\circ$.

It could be seen from (1) that the smaller the pore radius r is in the matrix, the higher the penetrating pressure of matrix P is. If the average radius of micropores in the matrix was less than 3.96 μ m [9], the matrix can be able to endure a pressure of 10⁵ Pa between anode and cathode. The LiAlO₂ powder in the slurry can be small enough to ensure the radius of micropores in the matrix is less than 3.96 μ m. It was generally believed that the optimum range of the ceramic particle size

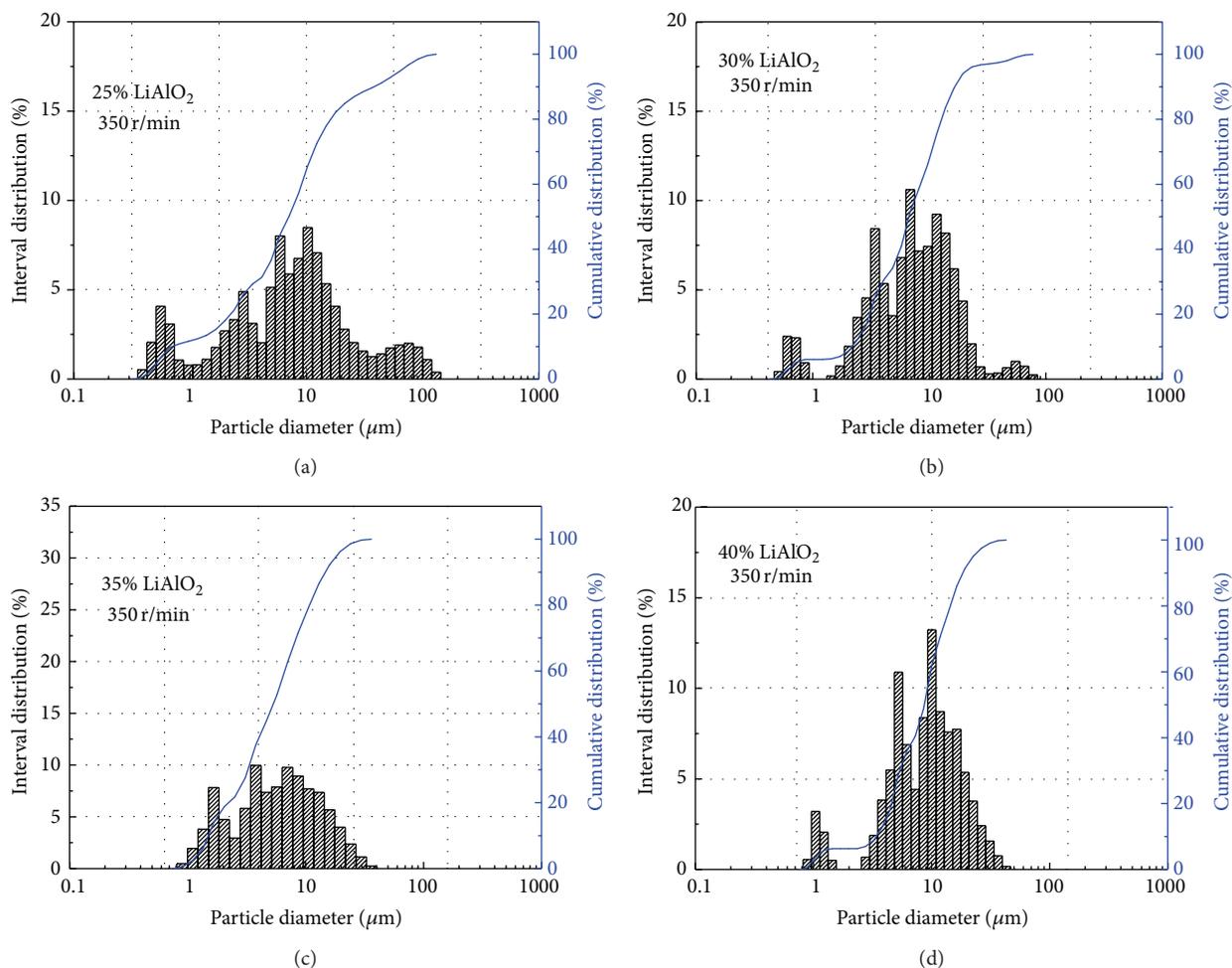


FIGURE 2: Particle analysis of slurries with different LiAlO₂ solid loading for milling time 17 h at milling speed 350 rpm. (a) 25%, (b) 30%, (c) 35%, and (d) 40% LiAlO₂ solid loading.

is in the range of 1–4 μm [10] and the specific surface area is in the range of 2–5 m²/g [11].

The mill speed and milling time had a significant impact on the distribution of powder particle size. The cumulative distribution of the powder particles of the same diameter increased rapidly while the speed increased, but too high speed could accelerate the wear of the milling balls. With the increasing of milling time, the powder particle size decreased gradually, the specific surface area of the powder particles increased gradually, and the surface energy and surface activity of the powder particles increase and thus cause agglomeration, which extends the milling time again and makes the cumulative distribution of the powder particles of the same diameter drop slowly [12].

The mass fraction of the LiAlO₂ powder in the slurry directly affects the rheology and particle density of the slurry. The lower the mass fraction was, the better the rheology was. Lower mass fraction is conducive to the improvement of milling efficiency. But too low mass fraction could reduce the collision of the powder particles with the milling media.

Particle size distributions in the slurries with different constituents mentioned above were shown in Figure 2.

It could be seen from Figure 2 that when the speed of ball milling was at 350 rpm, the average size of the particles in the four samples shown in the Figure 2 was larger than 3.96 μm. The lower the solid content of the slurry was, the wider the LiAlO₂ particle size distribution was. However the LiAlO₂ particle size distribution became narrower and the average particle size became smaller when the solid content increased. A possible explanation for this phenomenon could be that the collision opportunity for LiAlO₂ particles and grinding ball increased in a viscous liquid. According to the trend mentioned above, when milling time and milling speed increased, the average particle size of LiAlO₂ particles in the slurry became smaller and particle size distribution became narrower.

Figures 3 and 4 showed that particle size distributions of the slurries with 35% and 40% solid content, respectively, with milling speed increased to 450 rpm and the milling time increased to 24 h. As was evident in Figures 3 and 4, the LiAlO₂ particle average diameter decreased to 1.67 μm and 1.76 μm, respectively, and about 90% particle size was less than 4.0 μm. As increasing the speed and the milling time in the initial ball milling stage had a possible effect on the

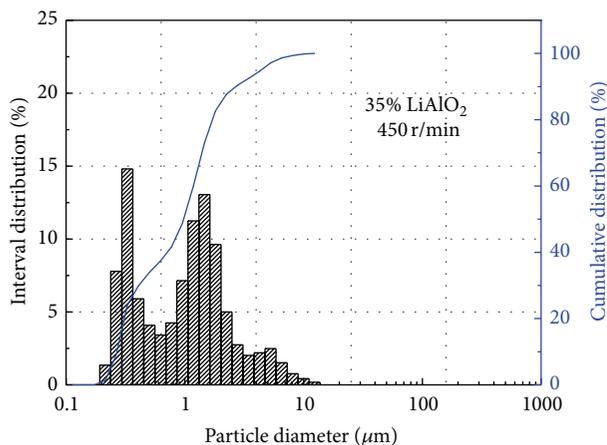


FIGURE 3: Particle analysis of the slurry with 35% LiAlO_2 solid loading for milling time 24 h and at milling speed 450 rpm.

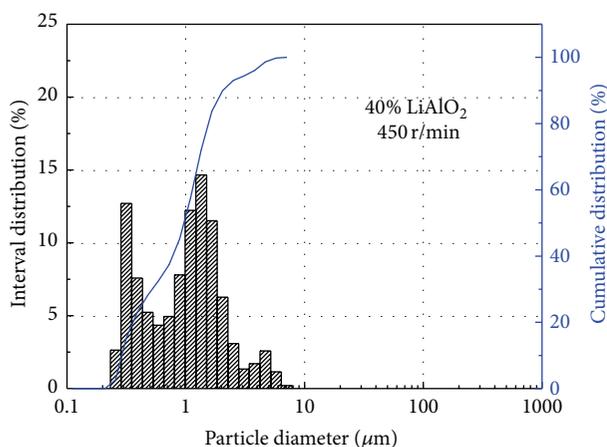


FIGURE 4: Particle analysis of the slurry with 40% LiAlO_2 solid loading for milling time 24 h and at milling speed 450 rpm.

particle size distribution in the slurry, one piece of green sheet could not prevent 0.1 MPa pressure difference between anode and cathode. Hot pressing several green sheets into one dense matrix was an effective method to reduce the defect and the big pore size in the matrix.

3.2. The Contents of Organic Compounds. The organic solvents could wet LiAlO_2 powder particles better than water-based solvents and prepare the slurry with lower viscosity and shorter drying time because of its good volatility [13]. The binder could wrap the powder particles, self-cure to form a surface to produce a strong three-dimensionally interconnected resin frame. It could increase the strength and toughness of green sheet [14]. The binder content in the slurry could increase with the content of LiAlO_2 powder. The plasticizer in the slurry could reduce the plastic limit temperature of the binder below room temperature, so that the binder had good fluidity and did not condense at room temperature [15]. The binder and the plasticizer were used together in the preparation of the slurry [16].

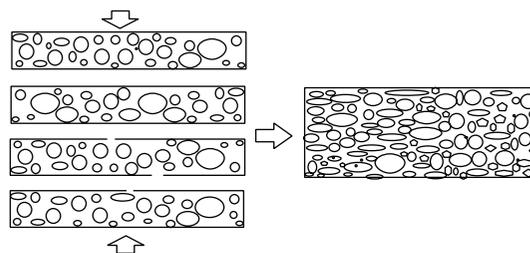


FIGURE 5: Pores brought about by piling up of different particles resulting in pressing.

An appropriate amount of plasticizer micromolecules was inserted in the polymer chains of the binder to increase the long-chain distance. It played a lubricating role and reduced the viscosity. The dispersant in the slurry could be adsorbed on the particle surface to prevent the powder particles from agglomerating. The dispersant reduced the viscosity of the slurry and improved its rheology mainly by increasing the repulsive potential energy or lowering the gravitational potential energy among the particles.

In the milling process, the binder and the dispersant could absorb and wrap the LiAlO_2 powder particles competitively; they affect the distribution uniformity and rheology of the particles in the slurry [17]. Therefore, the organic solvent, LiAlO_2 powder, and dispersant should be added firstly during the preparation of the slurry to wet the LiAlO_2 powder and break the aggregates via ball milling. In the mixing process, the dispersant was adsorbed on the LiAlO_2 powder particles to form a film, which prevents the particles from reaggregating. This caused the LiAlO_2 powder particles suspended in the slurry, as was a necessary prerequisite to play the best effect of the dispersant. The binder and the plasticizer were added after 10 hours of ball milling. Compound stability with the dispersant after being stirred was generated to maintain the LiAlO_2 powder particles in a suspended state. Finally, defoamer was added to enlarge the air bubbles in the slurry to the extent of rupture in the milling process. Alumina fibers were added to improve the mechanical strength of the matrices.

As presented in Table 1, the weight percentage of the organic compounds decreased with the increasing of LiAlO_2 solid loading. It indicated that the particles were less separated in the slurries. The contents of the organic compounds were decreased in the distances between LiAlO_2 particles in the matrices with the increasing of LiAlO_2 solid loading.

3.3. The Natural Piling Up of LiAlO_2 Particles. The mixture of $\gamma\text{-LiAlO}_2$ and $\alpha\text{-LiAlO}_2$ could be used in preparing matrix due to its property of keeping the initial phases composition in MCFC environment. Various size LiAlO_2 particles were piled up to produce good mechanical strength for matrix. The $\gamma\text{-LiAlO}_2$ powders were synthesized by boehmite, which could be used as coarse powders. $\alpha\text{-LiAlO}_2$ was used as a fine powder in the matrix slurry production. 2–10 wt.% of fine powder was added into the organic compounds at the beginning of ball milling processes, and 10–15 wt.% coarse

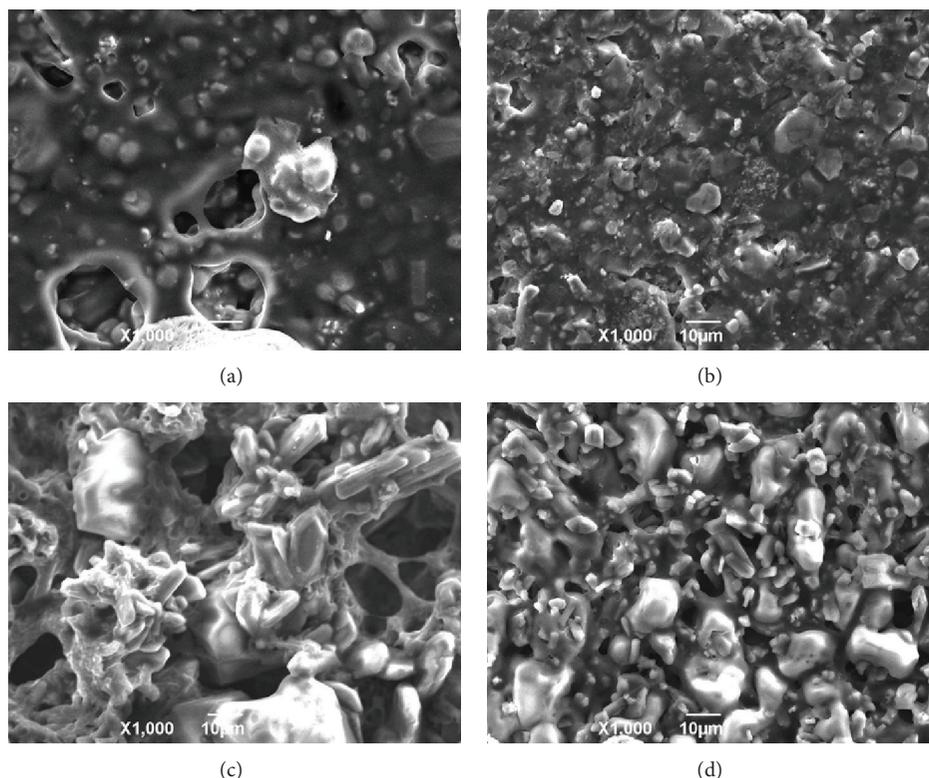


FIGURE 6: Morphologies of the green sheets with (a) 25%, (b) 30%, (c) 35%, and (d) 40% LiAlO_2 solid loading.

powder was added to the compounds in last stage of ball milling. Coarse powder became moderate by ball milling for long time. The fine, moderate, and coarse LiAlO_2 powders could pile up in the ceramic LiAlO_2 powder in the natural state of the matrix by the process mentioned above. As seen from Figure 5, one piece of green sheet had a loose structure and a low bulk density. So that it could not withstand the gas penetration pressure between the anode and the cathode of the MCFC. Multiple green sheets were pressed together. It could compensate for the defect of a single green sheet. A dense matrix with a narrower distribution of pore size and a much higher bulk density was achieved.

3.4. Green Sheet Morphology. It had been demonstrated that the particle size distribution of ceramic powders had a great influence on the performance of slurry. Micro- or submicro-ceramic powders were usually considered to be favorable to obtain a stable suspension with high solid loading. High solid loading and low viscosity of LiAlO_2 slurry were beneficial for casting during the matrix production process. Accordingly, it was important to maintain proper fluidity of the slurry by optimizing its solid loading. Figure 6 gives the morphologies of the green sheets with different solid loadings.

It could be seen that all the samples possessed homogeneous microstructure, but the samples showed apparent difference microstructures with the different solid loadings. The LiAlO_2 particles were connected by polymer network formed by the binder and organic additives. The network was considered to be responsible for the favorable strength

of green bodies. It is seen from Figure 6 that the LiAlO_2 particles were basically wrapped with the binder and other organic additives, which filled in the space between LiAlO_2 particles. The distance between the LiAlO_2 particles became smaller and smaller with the increasing of solid loading and the sharp decreasing of solvent. As shown in Figures 6(a) and 6(b), a large distance between the particles could result in large holes in the matrix after organic ingredients burned up. Higher solid loading could reduce the distance between the particles, as verified in Figures 6(c) and 6(d). The particle size was the smallest and uniformly distributed, when the solid loading was 40%. As the solid loading increased further, the slurry became thicker and pastier so that it was difficult to cast. Therefore, the slurry with 40% ceramic solid loading was better than the others. It could meet the requirements of the casting process.

3.5. Matrix Characterization. Based on the observations mentioned above, slurry composition with 40 wt.% ceramic powder was selected to produce the matrix for reasonable pore distribution and successful cell testing. The porosity and pore size distribution of the matrix were measured after burning out the organic ingredients in the matrix. The result of porosity analysis for the matrix is shown in Figure 7. The matrix had submicron pores in the range 0.1–0.4 μm and a porosity of 50 vol.%. It was consistent with the theoretical and technical requirements for the matrix.

To evaluate the matrix performance for gas sealing, a single MCFC was assembled. One matrix and two carbonate

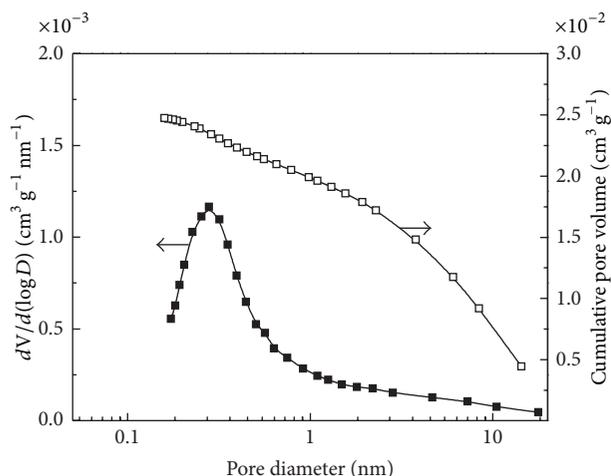


FIGURE 7: Pore size distribution of the matrix with 40% solid loading by the optimal process.

green sheets were stacked as a sandwich. Stainless steel end plates and the matrix with the carbonate sheets were assembled into a single cell. The matrix and the electrolyte sheets were sintered in situ under a specific heating program. The carbonates were molten at 480°C and immersed in the microholes in the matrix by capillary force. A measurement of gas crossover in the matrix was carried out when the temperature of MCFC rises to 540°C. The cathode inlet and the anode outlet were closed, and the nitrogen pressure of the anode inlet was gradually increased to test the gas crossover. Gas crossover in the matrix occurred when gas was released from the cathode outlet. When pressure was under the pressure required for the measurement of gas crossover in the matrix, gas crossover occurred. The test result showed that the gas crossover occurred when the nitrogen pressure difference reached 0.7 MPa. It was indicated that the matrix with 40% solid loading had a good performance. When the cell temperature rose to 650°C, if there was no gas crossover in the cell, the H₂ was supplied to the anode, and a gas mixture of 70 mol% air and 30 mol% of CO₂ was supplied to the cathode. The performance of the cell was tested by an electrochemical workstation. The results from electrical performance tests of the single cell were shown in Figure 8, where a maximum discharge current of 20 A at 0.56 V was used. The testing results demonstrated good performance of the matrix with 40% solid loading.

4. Conclusion

MCFC electrolyte matrices were prepared by tape casting. In order to optimise the production process of matrix, organic solvent, additives, and slurries with different solid loadings of lithium aluminate were used to prepare matrices green body. The result matrices green bodies were tested. Comparative results showed that particle size distribution of the slurries was determined by the solid loading amount and ball milling process. The slurry with 40% solid loading and ball milling condition of 450 rpm for 24 h was optimal for matrix casting.

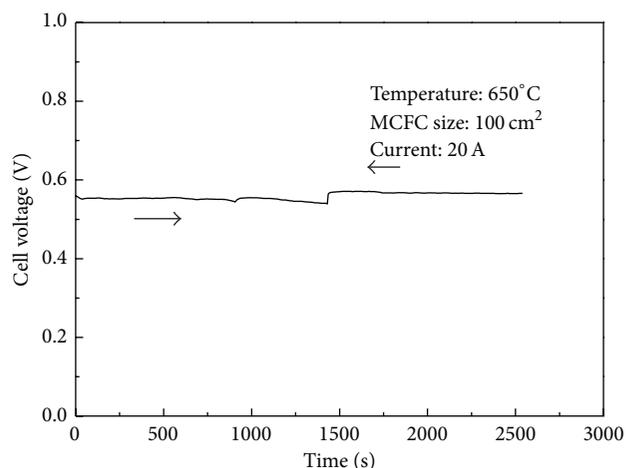


FIGURE 8: Discharging performance of a single MCFC with a matrix made of γ -LiAlO₂ and α -LiAlO₂ powders.

Pore size distribution and electrical performance testing of the cell verified that the matrix prepared by the optimal process performed well for gas prevention and cell discharging in MCFC.

Conflict of Interests

The authors declare that they have no financial or personal relationships with other people or organizations that can inappropriately influence their work; there is no professional or other personal interest of any nature or kind in any product, service, and/or company that could be construed as influencing the position presented in or the review of this paper.

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