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

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Received 27 February 2014; Accepted 26 March 2014; Published 23 April 2014

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 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, scanning electron microscopy, and BET surface area analyzer. The testing results showed that the matrix with 40% solid loading gave the maximum discharge current of 20 A at 0.56 V.

2. Experimental Method

2.1. Matrix Fabrication. The α-LiAlO 2 and γ-LiAlO 2 (1:1 molar ratio) [5] powders were used as the solid constituent
of MCFC matrix. The $\alpha$-LiAlO$_2$ and $\gamma$-LiAlO$_2$ powders were made from boehmite reacting with Li$_2$CO$_3$ 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 Al$_2$O$_3$ fiber as reinforced material. The slurry composition is given in Table 1.

The ratio of binder, solvent, plasticizer, dispersant, and LiAlO$_2$ powder in the slurry was varied to obtain LiAlO$_2$ powder loading in the range of 25–40 wt.%. The slurry was prepared by ball milling of LiAlO$_2$ 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 Al$_2$O$_3$ 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 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.

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

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Solid</th>
<th>Solvent</th>
<th>Binder</th>
<th>Plasticizer</th>
<th>Dispersant</th>
<th>Defoamer</th>
<th>Al$_2$O$_3$ fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>25</td>
<td>59</td>
<td>8</td>
<td>6</td>
<td>1.2</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>b</td>
<td>30</td>
<td>52</td>
<td>9</td>
<td>7</td>
<td>1.2</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>c</td>
<td>35</td>
<td>43</td>
<td>12</td>
<td>8</td>
<td>1.3</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>d</td>
<td>40</td>
<td>36</td>
<td>13</td>
<td>9</td>
<td>1.3</td>
<td>0.6</td>
<td>0.1</td>
</tr>
</tbody>
</table>

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 LiAlO$_2$ and the organic ingredients in the slurry. According to the Yong-Laplace equation [3]

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

(1)

$\delta$, coefficient of surface tension of the electrolyte, is 0.198 N·m$^{-1}$ and $\theta$, 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 micro pores in the matrix was less than 3.96 $\mu$m [9], the matrix can be able to endure a pressure of $10^3$ Pa between anode and cathode. The LiAlO$_2$ powder in the slurry can be small enough to ensure the radius of micro pores in the matrix is less than 3.96 $\mu$m. It was generally believed that the optimum range of the ceramic particle size
Figure 2: Particle analysis of slurries with different LiAlO$_2$ solid loading for milling time 17 h at milling speed 350 rpm. (a) 25%, (b) 30%, (c) 35%, and (d) 40% LiAlO$_2$ solid loading.

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 LiAlO$_2$ particle size distribution was. However the LiAlO$_2$ 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 LiAlO$_2$ 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 LiAlO$_2$ 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 LiAlO$_2$ 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
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].

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 $\gamma$-LiAlO$_2$ and $\alpha$-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 $\gamma$-LiAlO$_2$ powders were synthesized by boehmite, which could be used as coarse powders. $\alpha$-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
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 $\mu$m 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...
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 melted 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.

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.

Acknowledgment

This study was supported financially by the National Energy Bureau Project of the integrated gasification fuel cell power generation system development and demonstration (NY20130202-1).

References


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