A Study on the Performance of Matrix Prepared by Tape Cast and Its Molten Carbonate Fuel Cells (MCFCs)

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Abstract: The matrix prepared with γ-LiAlO₂ powder and by tape cast displayed higher ability of preventing from gas crossover and lower ohmic polarization. The voltages of the stack (three cells, 122 cm²) stacked with the matrix were 2.02 and 1.78 V at 200 and 246 mA/cm², respectively, and the output power reached 53.4 W. The cell (28 cm²) voltages were 0.85 and 0.75 V at 200 and 300 mA/cm², respectively, and the output power was about 6.6 W. Compensating the shrinkage of matrix in stacking cells promoted the enhancement of the MCFC performance.

Key words: Matrix, Compensating the shrinkage of matrix, Tape cast, MCFC performance

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1 Introduction

Increasing attention has been paid to the attractive advantages of MCFC: producing electricity with coal gas and natural gas, high efficiency, effective utilization of heat energy, free from contamination and noise, electrode catalyst of inexpensive metals, and so forth. MCFC is developing rapidly in the recent 20 years in some countries. MCFC with high capacity has been brought into a run, and 2MW-power generation system has been put in test run. However, some problems have arisen in the course of its progress, for example, corrosion of electrodes and cell materials at high temperatures. For commercialization of MCFC there are still some challenging
technical issues to be solved. These problems being resolved, MCFC will be a promising and clean power source device in the coming century.

Matrix is a key component of MCFC and can be prepared by many methods: thermo-compressing\(^{[1,2]}\), electrophoretic deposition\(^{[3]}\), vacuum casting\(^{[4]}\), cold- and hot- roll- milling\(^{[5,6]}\), tape cast\(^{[7,8]}\) and so on. Among them the tape cast can be applied not only to prepare the matrix with higher cell performance, but also to large-scale production condition. Furthermore this technique is simple and can be operated easily, and the quality of matrix is reproducible and reliable.

The objective of the present work is to research and develop MCFCs of long term, and with high capacity and high cell performance. The ability of retaining electrolyte in matrix plays a significant role. In this paper we report on the matrix prepared with\(\gamma\)-LiAlO\(_2\) powder of higher surface area and in definite fine/coarse powder ratio, which has demonstrated improved thermo-mechanics and higher ability of retaining electrolyte in MCFC.

The working principle and structure schematic of MCFC are the same as those reported in the previous literature\(^{[9,10]}\).

2 Experimental

2.1 Preparation of LiAlO\(_2\) powder

The powder with which the MCFC matrix is prepared is mostly\(\gamma\)-LiAlO\(_2\), while sometime it is also\(\alpha\)-\(\beta\)-LiAlO\(_2\)\(^{[5,6]}\). In this work the matrix was prepared with\(\gamma\)-LiAlO\(_2\) powder. Coarse\(\alpha\)-LiAlO\(_2\) powder was prepared by mixing Li\(_2\)CO\(_3\)+\(\alpha\)-Al\(_2\)O\(_3\) in 1:1 mol. ratio, reacted at 450-700 \(^\circ\)C for 20 - 30 h, and its particle size was 3 \(\mu\)m. Fine\(\alpha\)-LiAlO\(_2\) powder was prepared by the “Chloride” synthesis\(^{[11]}\), the resulting particle size was 0.33 \(\mu\)m. Coarse\(\gamma\)-LiAlO\(_2\) powder was prepared by baking the coarse\(\alpha\)-LiAlO\(_2\) powder at 900 \(^\circ\)C for 20 - 40 h, giving particle size of 4.0 \(\mu\)m. Then fine\(\gamma\)-LiAlO\(_2\) powder was prepared by baking the fine\(\alpha\)-LiAlO\(_2\) powder at 900 \(^\circ\)C for several h and the particle size of final powder was less than 0.18 \(\mu\)m.

2.2 Preparation of the matrix by tape cast

Firstly \(\gamma\)-LiAlO\(_2\) powder in a definite fine/coarse powder ratio was mixed with the binder PVB, plasticizer, solvent and so on. Then the mixture was ball-milled for 80 - 140 h into a paste with which the matrix was prepared by tape cast. The matrix in saturated solvent vapor was dried by controlling volatilizing velocity of the solvent\(^{[12]}\). The texture and thickness of matrices were uniform and without any cracks. These matrices were thermo-compressed into a cell matrix whose thickness was 0.6 - 0.7 mm and density was 1.75 - 1.85 g/cm\(^3\) under the conditions: 100 - 150 \(^\circ\)C, 1.0 - 3.0 MPa/cm\(^2\) and 2 - 5 min.

2.3 Stacking, starting and operating of MCFC.

A stack (three cells) was stacked with the matrices and sintered porous Ni-Cr and Ni plates (area, 122 cm\(^2\); thickness, 0.4 mm; average pore radius, 10.0 \(\mu\)m; porosity, 70 %) for the anode and cathode respectively, and a cell (28 cm\(^2\)) was assembled. The stack and cell were started
and operated by the manners as the same as those previously reported[10]. When the temperature was 650 °C, electrolyte (molten carbonate salts: Li$_2$CO$_3$ 0.62 + k$_2$CO$_3$ 0.38) became more smooth. Gas crossover in the cell was checked with nitrogen. If there was no gas crossover, the O$_2$ + CO$_2$ (O$_2$/ CO$_2$ = 40/ 60) and H$_2$ + CO$_2$ (H$_2$/ CO$_2$ = 80/ 20) mixture gases were introduced in the cathode and anode chamber respectively. When open-circuit potential increased to about 3.3 and 1.1 V for the stack and cell respectively, they were loaded to discharge and their performance were measured.

3 Results and discussions

3.1 Measuring the physical parameters of matrix.

According to the Yong-Laplace equation

\[ P = \frac{\delta \cos \theta}{\gamma} \]  

We could realize that the smaller the pore radius of matrix, \( \gamma \) is, the higher the penetrating pressure of matrix, \( P \) is from Equation (1) where \( \delta \) is the coefficient of surface tension of the electrolyte, and \( \theta \) is the contact angle between the matrix and the electrolyte. When temperature in the cell reaches at 650 °C = 0.198 NM$^{-1}$ for the electrolyte, \( \theta = 0^\circ \). According to the literature[13], a minimum pressure of 10$^5$ Pa is needed to prevent from mixing and crossover of fuel gas and oxidant. So average radius of micro-pores of matrix should be 1 \( \mu \)m or less, and maximum radius of micro-pores of matrix approximating 4 \( \mu \)m can be derived.

Again according to the equation:

\[ \rho = \rho_0 (1-C)^{-2} \]  

we could deduce the relation between the resistance of matrix and the percentage of LiAO$_2$ volume. \( \rho \) is the specific resistance of matrix and \( \rho_0 \) is the specific resistance of the molten carbonates(0.5767 Ω·cm$^{-1}$ at 650 °C), and \( C \) is the percentage of the LiAO$_2$ volume [(1-C) for the porosity of matrix]. As the concentration of organic compounds in matrix increases, the pore radius of the matrix becomes larger, the ability of preventing from gas crossover is lower, and the pore volume is increased, the more electrolyte is impregnated in matrix by the capillary force, the resistance of matrix decreases. As can be known from Equation (2), the resistance of matrix is inversely proportional to the square of porosity in matrix. It implies that the increase of porosity in matrix results in the decrease of the resistance in matrix more significantly than the decrease of thickness of matrix does.

Considering the two requirements mentioned above, the porosity in matrix should be more than 40 %, but less than 70 %. To check whether the prescription of matrix, the technique of matrix preparation and the heating rate in MCFC are reasonable or not, it is necessary to measure the maximum and average radii of micro-pores of matrix, pore distribution and porosity in matrix.

1) micro-pore configuration of the matrix surface
The SEM photographs of the surface and cross-section of matrix before burning out organic compounds are shown in Fig. 1. As been evident in Fig. 1, a great number of micro-pores on the matrix surface were revealed. Its average radius of micro-pores of the matrix ranged 0.10 - 0.30 \( \mu \text{m} \), and complicated micro-pore configurations were obviously in sight of the cross-section of matrix. Based on the SEM observation, the micro-pore configurations of surface and bulk of the matrix were integrated, they took important role in burning processes of the organic compounds in the matrix due to smooth diffusion of oxygen through a large number of micro-pores.

![SEM photographs of the surface and cross-section of matrix before burning out organic compounds in matrix](image)

2) Measuring the maximum pore radius and porosity of matrix

Maximum radius of micro-pores and porosity of matrix were measured by the penetrating and capacity methods respectively. The results are summarized in Table 1. The maximum radius of micro-pores and the porosity of matrix were determined to be 0.486\( \mu \text{m} \) and 20\%, respectively. However their values were increased to 4.86\( \mu \text{m} \) and 25\% respectively after drying matrix, because of some solvent remaining in the matrix volatilized in drying matrix. After thermal-compressing matrices the maximum radius of micro-pores and the porosity of matrices with three layers decreased, compared to those of matrix with single layer due to blocking up some channels (micro-pores) at the interface between three layers in matrices by thermal-compressing. Higher pressure of thermal-compressing brought out the smaller maximum radius of micro-pores and the lower porosity of matrices which were unfavorable to oxygen diffusion through micro-pores in matrices, but higher sticky strength to stick multiply layers strongly in matrices with which higher ability of prevent from cross-over of fuel gas and oxidant was benefit to electrochemical reaction in MCFC. Lower pressure of thermal-compressing brought out the maximum radius of micro-pores.
and the porosity of matrix almost unchanged, but too low sticky strength to stick multiply layers loosely in matrices. The maximum pores could be through straightly, the ability of preventing from crossover of fuel gas and oxidant was lower. The reasonable pressure of thermo-compressing, 1.8 - 2.4 MPa/cm² could be needed for keeping a large number of micro-pores and the higher porosity, at the same time bringing out the strong sticky strength between multiply layers in the matrices.

<table>
<thead>
<tr>
<th>Technique step</th>
<th>Thickness of the matrix/ mm</th>
<th>Number of the layers in the matrix</th>
<th>Used gas</th>
<th>Medium pressure/ MPa·cm⁻²</th>
<th>Minimum radius/μm</th>
<th>Maximum radius/μm</th>
<th>Porosity of the matrix/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before drying</td>
<td>0.16</td>
<td>1</td>
<td>N₂</td>
<td>H₂O</td>
<td>0.30</td>
<td>0.243</td>
<td>20</td>
</tr>
<tr>
<td>After drying</td>
<td>0.16</td>
<td>1</td>
<td>N₂</td>
<td>H₂O</td>
<td>0.03</td>
<td>2.43</td>
<td>25</td>
</tr>
<tr>
<td>After T. C.</td>
<td>0.18</td>
<td>1</td>
<td>N₂</td>
<td>H₂O</td>
<td>&gt;0.30</td>
<td>&lt;0.243</td>
<td>11</td>
</tr>
<tr>
<td>After T. C.</td>
<td>0.50</td>
<td>3</td>
<td>N₂</td>
<td>H₂O</td>
<td>&gt;0.30</td>
<td>&lt;0.243</td>
<td>11</td>
</tr>
</tbody>
</table>

Note: 1. T. C.: The thermal-compressing.

2. The measurements of the maximum radius of micro-pores and the porosity of matrix were conducted at 20 °C

3) The DTG curve of matrix

The dry matrix material was analyzed by the differential thermogravimetric method. The instrument used is a RT-20b thermogravimetric analyzing instrument made in Japan. The DTG curve of matrix prepared with γ-LiAlO₂ powder is shown in Fig. 2. Four segments are indicated on the curve. The weight loss in AB segment was 1 - 2 %, caused by the volatilization of anti-bubbling agent and some solvent remaining in the matrix when the temperature in air rises. The weight loss in BC, CD, and DE segments were produced by volatilizing and burning out plasticizer, binder PVB and tar (burnt residual) in their respective temperature ranges of the DTG curve, different from that of the matrix prepared with α-LiAlO₂ powder[10]. The BET surface area and internal pore volume of the former (mixed γ-LiAlO₂ powder), 7 M²/g and 0.002 cc/g were lower than those of the later (mixed α-LiAlO₂ powder), 11 M²/g and 0.01 cc/g. Lower BET surface area and internal pore volume of γ-LiAlO₂ powder could make volatilizing and burning out organic compounds, such as plasticizer, binder PVB and so on, clearly dependent on temperatures in their burning processes. From 200 to 360 °C, most mass of the organic compounds were volatilized. The total weight loss in the temperature range was 25 %, which made up 90 % of all weight loss. From 360 to 450 °C, only little organic compounds was volatilized and burnt, being tar burnt out
at the end of burning process. That cell was heated slowly preferably in 200-360 °C temperature range confirmed to the trends of DTG measurement.

4) Measuring the average radius of micro-pores, pore distribution and porosity in matrix

The sample (porous plate) was prepared by volatilizing and burning out the organic compounds in matrix under the simulating experimental conditions of slow heating and oxygen introduction in MCFC. It was measured by the mercury intrusion method. The instrument is CARLO ERBA STRUMENTAZION MICTOSTRUCTURE LABA 2000. The average radius of micro-pores of matrix was 0.10 - 0.20 μm. The porosity of matrix was more than 50%.

5) Measuring the maximum radius of micro-pores of matrix

Measuring the maximum radius of micro-pores of matrix after volatilizing and burning out the organic compounds in matrix is a simple means for checking the quality of matrix by the penetrating method. The results were calculated according to Equation (1) and are shown in Table 2. The average maximum radius of micro-pores of matrix, 0.354 μm could then be derived.

### Table 2

<table>
<thead>
<tr>
<th>dl/mm</th>
<th>gas</th>
<th>liquid</th>
<th>P/mm²</th>
<th>r[μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>N₂</td>
<td>alcohol</td>
<td>&gt; 0.12</td>
<td>0.326</td>
</tr>
<tr>
<td>0.4</td>
<td>N₂</td>
<td>alcohol</td>
<td>&gt; 0.140</td>
<td>0.381</td>
</tr>
</tbody>
</table>

Fig. 2 The DTG curve of matrix prepared with γ-LiAO₂ powder

Note: 1. Atmosphere: air
   2. 10 °C/min

3.2 Study on the conditions of assembling MCFC cells

1) Compensating the shrinkage of matrix.

The organic compounds in matrix were volatilized and burnt out during slow heating and introducing oxygen into the cells. The body of matrix was shrunken in the direction of stacking force perpendicularly to the cells. The results in measuring the shrunken matrix revealed that the shrinkage percentage of matrix was about 10 - 15%, and the shrinkage made the matrix thinner and poor ohmic contact between matrix and main components (electrodes, perforated plates, ...
rugged plates and other stacking hardware), at the same time the MCFC performance decreased. The dependence of MCFC performance on compensating the shrinkage of matrix is shown in Table 3. When the shrinkage of matrix was not compensated in stacking cells, the cell performance decreased. Contrarily, when it was compensated, the cell performance was improved. Increasing the thickness of the main components in MCFC could compensate the shrinkage of matrix. The increased thickness of main components in MCFC was equivalent to the shrunken thickness of matrix. So, after volatilizing and burning out the organic compounds in matrix at high temperatures the excellent ohmic contact between the shrunken matrix and the main components in the stacks and cells was maintained. Due to the thickness increase of main components in the stacks and cells, big gas leakage would be produced, so that the organic compounds in matrix would be volatilized and burnt out well and less easily carbonized. The short circuit between two electrodes would not bring out. The electrolyte could be impregnated in the bulk and seal face of matrix smoothly. These improvements in stacking and operating the cells would make them enhance the MCFC performance. Compensating the shrinkage of matrix in stacking cells promoted the enhancement of MCFC performance.

<table>
<thead>
<tr>
<th>Compensating the shrinkage of matrix in assembling cell</th>
<th>Cell voltage/V</th>
<th>200 mA/cm²</th>
<th>300 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>0.782</td>
<td>0.646</td>
<td></td>
</tr>
<tr>
<td>Halfway (only at anode side)</td>
<td>0.825</td>
<td>0.702</td>
<td></td>
</tr>
<tr>
<td>Wholly (at two electrode sides)</td>
<td>0.867</td>
<td>0.753</td>
<td></td>
</tr>
</tbody>
</table>

3) Dependence of MCFC performance on stacking pressure

All components in MCFC are thermo-expanded, being heated at high temperatures in operation of MCFC, so 25-30% of pressures loaded on the matrix go beyond those designed previously in stacking cells. That demands the matrix to be pressure-resistant under dynamic state. In our experiments the MCFC performance altered from 0.870 to 0.889 V at 200 mA/cm², from 0.739 to 0.760 V at 300 mA/cm², respectively, as the stacking pressure varied from 0.65 to 1.45 MPa/cm². It was revealed that the MCFC performance was independent of assembling pressure loaded upon matrix in the stacking pressure range (0.65 - 1.45 MPa/cm²), implying that the mechanical strength of matrix resisting to pressure lash was improved and the matrix had higher mechanics, at the same time it coincided well with the dynamic pressure at high temperatures.
3.3 MCFC performance

1) I-V performance curve

Two groups of I-V performance curves for the stack (three-cells, 122 cm$^2$) and cell (28 cm$^2$) of MCFC are shown in Fig. 3. Reaction gas pressure increased continuously, the stack and cell performance became higher reasonably. It illustrated that the matrix possessed a higher ability of preventing from gas cross-over. The stack voltage were 2.01 and 1.78 V at 200 and 246 mA/cm$^2$, respectively, and the output power was 53.4W. The cell voltage were 0.85 and 0.75 V at 200 and 300 mA/cm$^2$, respectively, and the output power was 6.6W.

We could see from Fig. 3 that the performance decrease nonlinearly due to active polarization, current density being less than 50 mA/cm$^2$. they decrease linearly due to ohmic polarization$^{[9]}$ in 50-200 mA/cm$^2$ current density range. Ohmic polarization includes the common effects of resistance of anode, cathode and matrix. The stack resistance, 16 nΩ and the cell resistance, 39 nΩ are derived from their I-V performance curves. However, the resistance of matrices are only 1.1 and 4.9 nΩ for the stack and cell respectively. So most part of ohmic polarization comes from the first cathode, the secondary anode and matrix.

2) The MCFC performance altering with thermal cycle number

When the cell started to be operated the temperature rose from R. T. to 650 °C, as the cell was going to be stopped, the temperature lowered from 650 °C to R. T., that completed a thermal cycle. The MCFC performance altering with thermal cycle number is present in Table 4. The MCFC performance altered from 0.868 to 0.886 V at 200 mA/cm$^2$, from 0.750 to 0.754 V at 300 mA/cm$^2$ for 8 thermal cycles respectively, indicating that the MCFC performance had not decreased for the thermal cycle number, and that there were no cracks and gas crossover in the matrix after repeatedly cold and hot lash, illustrating further that the matrix had excellent thermomechanics.
Tab. 4 The MCFC performance altering with thermal circle number

<table>
<thead>
<tr>
<th>Thermal circle number</th>
<th>P (MPa/cm²)</th>
<th>200 (mA/cm²)</th>
<th>300 (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9</td>
<td>0.868</td>
<td>0.750</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>0.892</td>
<td>0.762</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>0.874</td>
<td>0.750</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>0.896</td>
<td>0.776</td>
</tr>
<tr>
<td>6</td>
<td>0.9</td>
<td>0.854</td>
<td>0.735</td>
</tr>
<tr>
<td>8</td>
<td>0.9</td>
<td>0.886</td>
<td>0.754</td>
</tr>
</tbody>
</table>

Note: 1. Fuel gas and oxidant utilization: 20%.
2. Anode: Ni–Cr, cathode: NiO.

3) The dependence of MCFC performance on fuel gas and oxidant utilization

The dependence of MCFC performance on fuel gas and oxidant utilization differ from each other. As shown in Fig. 4, when fuel gas utilization increased and oxidant utilization was stable at 20%, the MCFC performance decreased. The ratio of H₂/CO₂ decreased from 80/20 at the inlet of anode chamber to lower one with increasing fuel gas utilization and with increasing concentration of reaction products H₂O and CO₂. The MCFC performance declined according to the Nernst equation and due to higher concentration polarization of high CO₂ and H₂O concentration in the fuel mixture gas. When oxidant utilization increased and fuel gas utilization was stable at 20%, the MCFC performance became higher. The ratio of O₂/CO₂ increased from 40/60 at the inlet of cathode chamber to lightly higher one with increasing oxidant utilization due to depletion ratio of O₂/CO₂ = 1/2 in the cathode reaction, thus by contrast the MCFC performance was higher.

4) The dependence of MCFC performance on temperature

In our experiments, the dependence of MCFC performance on temperatures is shown in Fig.
5. At 680 °C, open circuit potential (OCP) decreased according to the Nernst equation, at the same time volatilizing of the electrolyte influenced the transportation of the electrolyte in matrix. But the MCFC performance increased linearly with elevating temperature at 200 and 300 mA/cm² respectively because of the decrease of active polarization in electrodes, concentration polarization of reactants and electrolyte, and increase of ionic conductance. At lower temperatures of 610 and 620 °C (at 200 and 300 mA/cm² respectively) the transportation of the electrolyte in matrix slowed relatively, the MCFC performance altered linearly with a little influence of concentration polarization. Two lines at 200 mA/cm² and 300 mA/cm² respectively were paralleled to each other in the temperature range. It implied that the transportation of the electrolyte in matrix coincided with operating cells at high current density in wide temperature range.

Conclusion

MCFC matrix has been prepared with γ-LiAlO₂ powder and by tape cast. The reasonable physical parameters were the average pore radius of 0.10 - 0.30 μm, the porosity of more than 50 % and so on, the stack (three cells, 122 cm²) voltages were 2.01 and 1.78 V at 200 and 246 mA/cm², respectively, and the output power reached 53.4 W. The cell (28 cm²) voltages were 0.85 and 0.75 V at 200 and 300 mA/cm², respectively, and the output power was about 6.6 W. All displayed that the matrix had a higher ability of preventing from gas crossover and a lower ohmic polarization. Its quality was reproducible and reliable, and the preparation technique was simple and could be operated easily. Compensating the shrinkage of matrix in stacking cells promoted the enhancement of the MCFC performance.

References: