Study on the Preparation Process and Influential Factors of Large Area Environment-friendly Molten Carbonate Fuel Cell Matrix

Ruiyun Zhang, Shisen Xu, Jian Cheng, Hongjian Wang and Yongqiang Ren
China Huaneng Clean Energy Research Institute, Beijing 102209, China
E-mail: zhangruiyun@hnceri.com

Abstract. Low-cost and high-performance matrix materials used in mass production of molten carbonate fuel cell (MCFC) were prepared by automatic casting machine with α-LiAlO2 powder material synthesized by gel-solid method, and distilled water as solvent. The single cell was assembled for generating test, and the good performance of the matrix was verified. The paper analyzed the factors affecting aqueous tape casting matrix preparation, such as solvent content, dispersant content, milling time, blade height and casting machine running speed, providing a solid basis for the mass production of large area environment-friendly matrix used in molten carbonate fuel cell.

1. Introduction
The fuel cell is a kind of power generation device which directly converts the chemical energy of the fuel into electric energy [1]. Unlike the traditional coal-fired power generation technology, the fuel cell adopts electrochemical catalysis to convert the chemical energy in the fuel directly into electric energy, which go beyond the heat engine Carnot cycle efficiency limit because there’s no thermodynamic cycle, and the current total efficiency of fuel cell is between 45% to 60%. The molten carbonate fuel cell (MCFC) is a high temperature fuel cell working at 650 ℃ developed in the late 1950s. The waste gas generated by the cell stack can be combined with the gas turbine or steam turbine to further recover the heat, and the total efficiency is more than 80%, and the power generation efficiency is higher than that of the thermal power plant, and its environmental performance is better than conventional thermal power plants. With many advantages, fuel cell is considered to be the fourth largest energy conversion power generation system after the thermal power generation, hydropower and nuclear power generation, and can be an alternative power plant of the internal combustion engine[1]. It will be the most attractive green energy known as the 21st century.

On December 2, 2015, delegates at the Ninth China-Japan Energy Conservation and Environmental Protection Forum enthusiastically discussed all of the clean coal power generation technologies from now until 2030 as shown in Fig. 1, including ultra supercritical thermal power technology (A-USC) (power generation efficiency about 46%), 1700 ℃ level IGCC (power generation efficiency about 46 ~ 50%), the overall coal gasification fuel cell power generation technology (IGFC) (power generation efficiency of 55%) , as well as the innovative IGFC. As of all those power generation methods, fuel cell was regarded as the most ideal distributed power generation for its advantages of good modular, and higher power generation efficiency at lower power.
Among the many fuel cells, MCFC is believed to have good practical prospects, and is the mainstream of the current study. MCFC has porous nickel as an anode, porous nickel oxide as a cathode, an eutectic mixture consisting of Li$_2$CO$_3$/K$_2$CO$_3$ or Li$_2$CO$_3$/Na$_2$CO$_3$ as an electrolyte, and the molten electrolyte is dispersed in matrix prepared by $\alpha$-LiAlO$_2$ or $\gamma$-LiAlO$_2$ powder. Matrix is one of the core components of MCFC with the function of electronic insulation, ion conduction, gas seal and so on. Therefore, matrix must have high strength, be able to bear high temperature molten salt corrosion, could block the gas through when immersed in molten salt electrolyte, and could have good ionic conductivity. The performance of matrix is closely related to its porosity and average pore size. The larger porosity and average pore size is, the more electrolyte immersed in the matrix, then the matrix resistance becomes small. But the average pore size is large, so it may have the risk of channeling gas between cathode and anode. Therefore, it is required that the matrix has a reasonable porosity and pore size distribution, the general porosity required is of 50% to 70%, pore size is less than 1μm, and has a good distribution. This paper studied a simple and environment-friendly matrix preparation method, $\alpha$-LiAlO$_2$ powder synthesized by solid-state reaction method and polyvinyl alcohol (PVA) are blended together, with distilled water as solvent, to form a slurry which is put into the automatic casting machine to make water-based matrix.

2. Experiments

2.1. Preparation of $\alpha$-LiAlO$_2$ Powder by Solid State Reaction

After many experiments, the LiAlO$_2$ was chosen as a matrix material. LiAlO$_2$ has many kinds of crystal form, the most common are $\alpha$, $\beta$ and $\gamma$ type, usually $\alpha$-LiAlO$_2$ is more stable under high pressure, $\gamma$-LiAlO$_2$ is more stable at high temperature, and $\beta$-LiAlO$_2$ is a transition state and is not stable[1]. $\alpha$-LiAlO$_2$ was prepared by sol-gel solid-phase reaction method that alkaline alumina and lithium carbonate were mixed by equimolar ratio and calcined at 750℃. The reaction process was as follows:

$$\text{Al}_2\text{O}_3 + \text{Li}_2\text{CO}_3 = 2\text{LiAlO}_2 + \text{CO}_2$$

Fig. 2 shows the XRD patterns of the prepared $\alpha$-LiAlO$_2$ powder samples. Fig. 3 shows the particle size distribution of the $\alpha$-LiAlO$_2$ powder.
It can be seen from Fig. 2 and Fig. 3 that the α-LiAlO$_2$ powder prepared by the solid-phase reaction of the gel has a high purity and whose relative content reaches 96.58%, the equivalent particle diameter D10 is 2.6μm, the average particle diameter D50 is 7.53μm, the maximum particle size is 21.23μm, which has reached the requirements of MCFC matrix [2].

2.2. Preparation of MCFC Matrix

There are many methods for preparing MCFC electrolyte matrix: hot pressing, electrophoretic deposition, vacuum casting, hot and cold rolling and strip casting (casting method) and so on, the key is how to prepare high quality slurry. Large experiments show that large-scale water-soluble and environmentally friendly MCFC matrix can be prepared by using automatic casting machine, the preparation process shown in Fig. 4.

Fig. 5 shows the prepared large area of MCFC water-soluble matrix, the average thickness is of 0.8mm, the porosity is of 66.2% measured by mercury intrusion, the average pore size is of 0.2μm, the overall performance is ideal.
2.3. Matrix performance test

The prepared matrix, the sintered nickel electrode and the carbonate electrolyte salt are assembled to be a molten carbonate fuel cell unit to test the electrochemical performance of the prepared matrix. The assembly diagram and the physical drawing are shown in Fig. 6.

![Diagram of MCFC](image)

(a) The assembly diagram of MCFC  (b) The picture of test field

Figure 6. The molten carbonate fuel cell unit assembly

The assembled molten carbonated fuel cell was heated by electric heating at room temperature to 923K according to a certain temperature rise curve. In the 813K, H\textsubscript{2} was introduced into the MCFC anode, and the air and CO\textsubscript{2} were introduced into cathode, and electrochemical reaction occurs, resulting in open circuit voltage. After 923 K, electronic load was accessed to test cell discharge performance [3], [4].

Using the electrochemical workstation produced by German Zanner company to test its performance and long-term stability, the test results shown in Fig. 7 and Fig. 8.

![I-V curve test](image)

Figure 7. The I-V curve test of MCFC single cell

![Diagram of MCFC long discharge](image)

Figure 8. The diagram of MCFC long discharge

It can be seen from Fig. 7 and Fig. 8, at the discharge voltage of 0.75V, the discharge current density of the assembled single cell reached 120mA/cm\textsuperscript{2}, after nearly 350 hours of continuous operation, the
performance is basically stable, indicating that the prepared matrix has good electrochemical properties and could fulfill the requirements of MCFC power generation.

3. Influencing Factors of Preparing matrix by Water-based Tape Casting

3.1. Effect of solvent
Water-based casting was carried out using demonized water as the solvent during the experiment. The amount of water content, not only affects the viscosity of cast slurry, but also seriously affects the sedimentation properties and the thickness control of the later casting process. At the same time, the solvent content should also take into account with the dispersant, binder, plasticizer solubility relationship. Table 1 shows the effect of different solvent contents on the casting effect [5], [6].

Table 1. The effect of different solvent content on the casting

| Solvent content | Casting effect |
|-----------------|---------------|
| Less than 20%   | The slurry is not uniform and is dry. |
| 20~30%          | Cast film cracking, and the green body is difficult to remove from the polyester film. |
| 30~35%          | The slurry is relatively uniform, cast paste thickness is better control. |
| More than 35%   | The slurry is not uniform, casting process can not control the thickness of the matrix |

As can be seen from Table 1, when the solvent content is in the range of 30~35%, it doesn’t occur the deposition phenomenon, and the slurry is more uniform, it could be better control the thickness of the green body to achieve experimental purposes. So the amount of adding demonized water should be 30 to 35% during the experiments [7]-[11].

3.2. The effect of amount of dispersant added and milling time
In the slurry system, the function of dispersant is to disperse the powder particles in the slurry, so that the binder, plasticizer could better wrap particles to achieve the desired effect. Dispersant not only can enhance the solid capacity, but also has the function of weakening the viscosity of the slurry. In the experiments, lactic acid and citric acid were used as dispersants. The results showed that the milling time required was controlled between 45-48 hours when lactic acid as the dispersant, while the milling time was controlled between 20-24 hours when the citric acid as the dispersant [12], [13].

3.3. Scraper height and tape speed on the film formation

![Figure 9. The relationship between blade height and matrix thickness](image)
In the preparation of large area MCFC matrix, the scraper height and tape speed determines the thickness of the film after drying. Experiments shows that when the transport speed was 0.15m/s, the drying temperature was 50 °C. The results are shown in Fig. 9.

From the fig. 9 we can see that although the thickness of the film is increased with the height of the scraper, it fluctuated when the blade thickness is in the range of 1.0~1.5mm. We hope that the prepared single matrix be thinner so that good gas barrier could still be kept after hot pressed together of many single films, which is beneficial to the open circuit voltage and power. In this case, the height of the scraper is controlled at 1 mm, and the thickness of the dried film is about 0.2 mm. We have 5 to 6 sheets of film heated at 90°C and pressed at 50kg/cm^2, and the final matrix is produced whose thickness is of about 1.0mm, with a strong gas barrier properties[14], [15].

4. Conclusions
The large area environment-friendly Molten Carbonate Fuel Cell matrix was prepared by the automatic casting machine and the overall performance is ideal. The molten carbonate fuel cell unit was assembled with the prepared water-based matrix and the discharge test was carried out. The test results showed that the prepared matrix can be used for MCFC power generation. It is believed that the MCFC has good practical prospects and further optimizing the porosity and long lifetime test of larger area matrix are needed to promote China's MCFC industry.

Acknowledgments
This work was financially supported by Beijing Municipal Science & Technology Commission in the Future Science & Technology Park (Development of 20kW molten carbonate fuel cell power generation system) (TZ-16-BJKW01).

References
[1] Yi Baolian. Fuel Cell-theory technology application [M]. Beijing: Chemical Industry Press, 2004(in Chinese).
[2] Cheng Jian, Guo Liejin, Xu Shisen, et al. Preparation of α-LiAlO2 powder for MCFC by gel-solid method and its’ characteristics [J]. Proceedings of the CSEE, 2013, 33(s1): 148-152(in Chinese).
[3] Cheng Jian, Guo Liejin, Xu Shisen, et al. Key components of molten carbonate fuel cell matches and its performance diagnostic [J]. Proceedings of the CSEE, 2012, 32(s1): 101-107(in Chinese).
[4] U. S. Department of Energy Office of Fossil Energy, Morgantown Energy Technology Center, Fuel Cell Handbook, January 1994.
[5] Antolini E. The stability of LiAlO2 powders and electrolyte matrices in molten carbonate fuel cell environment [J]. Ceramics International, 2013, 39(4): 3463-3478.
[6] Choi H J, Lee J J, Hyun S H, et al. Fabrication and performance evaluation of electrolyte-combined α-LiAlO2 matrices for molten carbonate fuel cells[J]. International Journal of Hydrogen Energy, 2011, 36(17): 11048-11055.
[7] Zhang J, Zhang X, Tu M, et al. Preparation of core(Ni base)-shell(Silicalite-1) catalysts and their application for alkali resistance in direct internal reforming molten carbonate fuel cell[J]. Journal of Power Sources 2012, 198(1):14-22.
[8] Cheng Jian, Xu Shisen, Shu Kai. Test study on power generation from molten carbonate fuel cells[J]. Thermal Power Generation, 2010, 39(6):11-13(in Chinese).
[9] Huang Bo, Zhu Xinjian, Yu qingchun, et al. kW- class molten carbonate fuel cell stack[J]. Scientia Sinica Chimica, 2011,41(12):1884-1888(in Chinese).
[10] Lin Huaxin, Zhou Li, Ming Pingwen, et al. Influence of MCFC stacking pressure on matrix performance [J]. Battery Bimonthly, 2007, 37(1):6-8(in Chinese).
[11] Zhou Li, Yi Baolian, Cheng Mojie, et al. Study on kW-scale molten carbonate fuel cell stacks[J]. Battery Bimonthly, 2002, 32(3):138-141(in Chinese).
[12] Patil K Y, Yoon S P, Han J, et al. Phase stabilities in molten Li-K carbonate of efficient matrix materials for molten carbonate fuel cells thermodynamic calculations and experimental investigations[J]. Journal of Material Science, 2011, 46(8):2557-2567.
[13] Zhou L, Lin H, Yi B, et al. Study on a new structure of the separator plate assembly for molten carbonate fuel cell (MCFC) stacks[J]. Chemical Engineering Journal, 2007, 125(3):187-192.
[14] Wang Pengjie, Cheng Jian, Zhang Ruiyun, et al. Preparation and test of electrolyte film in molten carbonate fuel cell[J]. Thermal Power Generation, 2015, 44(12):42-45 (in Chinese).
[15] Zhou L, Lin H, Yi B, Zhang H, Shao Z, Ming P, Cheng M. A study on the start-up and performance of a kW-class molten carbonate fuel cell (MCFC) stack [J]. Electrochimica Acta 2006; 51:5698.