

A noble method for molten carbonate fuel cells electrolyte manufacturing

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Abstract An economic process for manufacturing of molten carbonate fuel cells was developed. This process consisted of fabricating the matrix by simply cutting it from a highly porous part with the geometry like an insulator brick, brush painting of the cathode layer followed by sintering and deposition of anode layer through thermal spray process. In order to manage the electrolyte content in the matrix and electrodes, coating of outer surfaces of the produced matrix with alumina slurry provided the required pores with small size at the interfaces with the electrodes. The polarization curves of the cells with alumina slurry coating and without it were not significantly different. The produced layer with small pores at the matrix outer surfaces caused the vaporization of the molten carbonate salt electrolyte to be reduced from 22.9% to 14.4% of initially infiltrated in salt weight content within 100 h of heat treating at 650 °C. This is at the same time to have the benefit of larger supply of electrolyte due to the application of highly porous matrix.

Keywords Molten carbonate fuel cell · Slurry method · Thermal spray · Porosity

Introduction

Molten carbonate fuel cells (MCFCs) are high-temperature fuel cells with an operating temperature about 600–700 °C. This temperature zone is ideal for internal reforming of

hydrocarbon fuels and exploitation of useable heat, while it is not too high to prevent application of cheap steel components. In addition, for solid oxide fuel cells operating at temperatures higher than abovementioned range, the Nernst voltage is decreased. Therefore, the operating temperature range of MCFCs makes a compromise between the advantages of a high-temperature fuel cell and technological considerations [1].

The operation principle of an MCFC fed with hydrogen as fuel is depicted in Fig. 1. The electrolyte of MCFC consists of a molten carbonate salt mixture (normally a eutectic mixture of 62 wt.% lithium and 38 wt.% potassium carbonates with a melting point around 550 °C). This salt mixture is impregnated into a solid porous matrix made from lithium aluminates (LiAlO_2). Contrary to other types of fuel cells, carbon dioxide should be supplied to the cathode along with oxygen and at the anode the same amount of carbon dioxide in terms of moles is released. The anode of MCFC at its current status is a porous layer of Ni–Cr/Ni–Al/Ni–Al–Cr and the cathode is a porous layer of lithiated NiO.

The major advantage of MCFC over other types of fuel cells is its high electrical efficiency at 50–60% [2]. The polarization curve of MCFCs is linear and the steepest among other types of fuel cells [3]. So, MCFCs are the most efficient fuel cells in low-current density range up to 150 mA cm⁻². MCFCs have one of the thickest electrode–electrolyte assemblies among all fuel cell types [4]. As a conclusion, they are normally designed for medium-scale stationary units for heat and distributed power generation.

Although the material costs of MCFCs are relatively low, there are challenges in reducing degradation of the materials to attain proof lifetime of the cells [5]. In fact, the efficiencies of power plants employing advanced turbine systems and gas turbine combined cycle are

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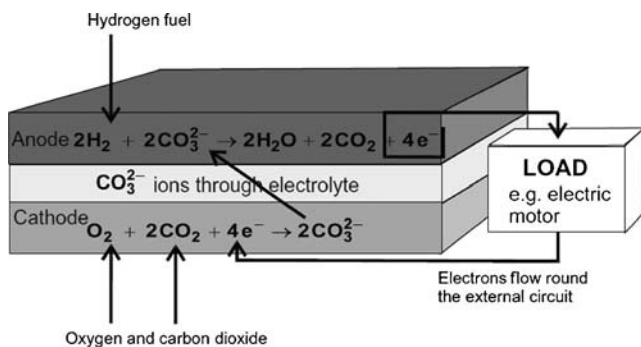


Fig. 1 Operation principle of MCFC

comparable to those for MCFC power generators. However, conventional turbines are commercially well known and their lifetimes are far longer than MCFC generators [6, 7].

There are many problems contributing to degradation of MCFC's performance in the course of operation cycle which suppress the commercialization of MCFCs, namely: NiO dissolution at the cathode; corrosion, creep, and sintering of the anode; matrix cracking; and electrolyte loss [8]. The electrolyte loss occurs by corrosion of components, creepage, reaction with cell components, and direct vaporization. This phenomenon diminishes the effective contact area of the electrodes with the electrolyte and results in reduced electrochemical reaction area, high ohmic resistance, and gas crossover or leakage [9]. The electrolyte content in each porous layer is determined by pore-size distribution in the layers. The electrolyte matrix should contain the smallest pores in order to be filled with the electrolyte while the electrodes pores are larger to be partially filled with the electrolyte and allow the gases to reach the reaction areas.

In this paper, the manufacturing process of an MCFC with pore-size gradient in the matrix thickness direction is described. The pore size at mid-thickness of the developed matrix is larger than the pore size at the interfaces with the electrodes. This arrangement enhances the volume of impregnated carbonate salt in the matrix for sustainable performance through diminishing vaporization, while preventing gas leakage through the matrix and ensuring good efficiency for the cell.

Manufacturing processes

Manufacturing of the matrix

The porous matrix was cut from an insulator brick made of partially sintered refractory compounds as presented in Table 1. The porosity of the brick piece that its micrograph section is shown in Fig. 2 was measured through

Table 1 Chemical composition of the insulator brick

Constituent	Weight percent
Calcined kaolin	45
Aluminum oxide	18
Calcium aluminate cermet	15
Crystalline silicate (cristobalite)	<10
Crystalline silicate (quartz)	<1

Archimedes' method as 41%. The dimensions of the sawed piece were $100 \times 100 \times 4$ mm. Thickness of the sawed piece was further reduced by polishing with no. 300 abrasive paper to 2 mm. Then, all of the surfaces of the piece were coated with a slurry method to produce a surface with reduced pore size and enhanced surface finish (Fig. 2). In order to prepare the slurry, alumina powder (99.5% purity, particle size $<10 \mu\text{m}$) was mixed with 5 wt.% anhydrous aluminum silicate ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, Merck 1.04440.2500, kaolin powder) and 10 wt.% ball clay (50% Al_2O_3 , 35% Fe_2O_3 , 6% SiO_2 , and 1.1% TiO_2 with particle size $<2 \mu\text{m}$). The last two substances were added to reduce the sintering temperature of the compound and attain good dispersion of particles. The compound was mixed at the ratio of 1 kg powder to 1,000 ml water and 100 ml wood glue (as a pore maker). Then ball milling was carried out for 6 h to form homogenous slurry.

Cathode layer

The cathode layer was produced by paint brushing nickel oxide powder (particle size $<10 \mu\text{m}$) on one face of the matrix which has already been coated with the slurry.

Process sintering

The matrix with the surfaces coated with the slurry and the cathode layer paint brushed was process sintered.

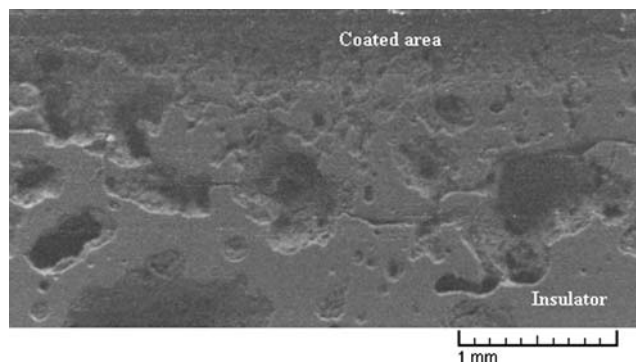


Fig. 2 Micrograph showing insulator brick section

The process parameters included firing the piece at 1,400 °C for 4 h. The micrograph of the matrix area coated with the slurry is shown in Fig. 3. Average depth of 0.4 mm and porosity of 27% were measured for this area through an image analyzing process. Figure 4 depicts the cathode layer produced by paint brushing NiO and sintering.

Impregnation with carbonate salts

Lithium, potassium, and sodium carbonates with a weight ratio of 62/36/2 were mixed and spread over the side of the electrolyte facing to the anode layer (which was not deposited yet). The area density of the applied salt mixture was $1.5 \times 10^{-4} \text{ kg cm}^{-2}$. The salt mixture was infiltrated into open porosities of the electrolyte after being melted at a temperature of 650 °C in furnace.

Anode layer deposition

The anode layer was produced by flame spraying of nickel aluminum powder (Sulzer-Metco, amdry 956 Ni + 5% Al) by a MK74 Metallisation torch with the supplied parameters from the torch manufacturer except for a standoff distance of 35 cm which was increased to result in a porosity of 31% as depicted in Fig. 5. During the thermal spray process, the substrate was cooled by a cooling jet of air exiting from a nozzle 1 mm in diameter with a back pressure of 1.5 bars in order to prevent melting of the impregnated salt mixture in the matrix. The anode layer coating was well sealed employing a strong glue to prevent digging of loose particles during the polishing stage of metallographic sample preparation.

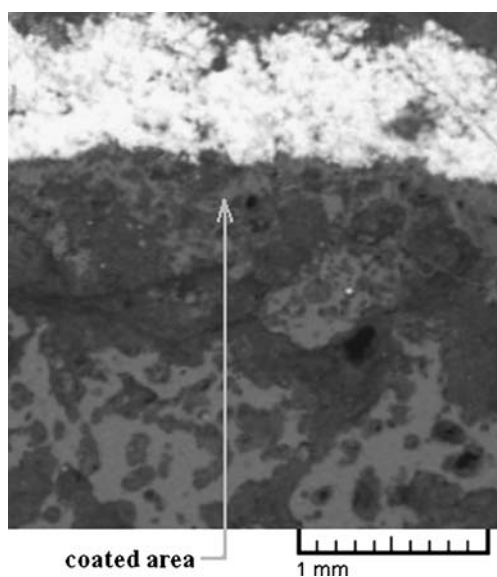


Fig. 3 Micrograph showing the area coated by slurry method

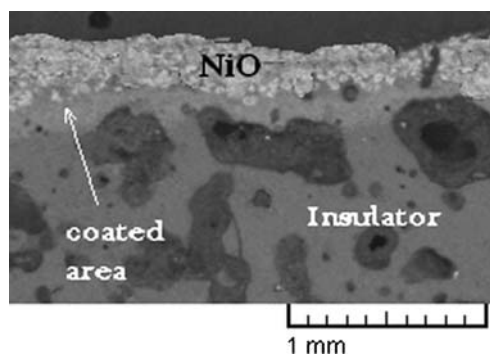


Fig. 4 Micrograph showing the NiO cathode layer after sintering

Cell testing

The current collectors shown in Fig. 6a were manufactured by machining a set of grooves as gas channels on 430 stainless steel plates. Also two manifolding parts (not shown) located at the channels ends provided sealing of gases and entrances and exits for them. The produced mats on the current collectors were put into electric contact during the test.

Dimensions of the cell are depicted in Fig. 6b. The single cell and current collector assembly were placed in an electric furnace in order to hold constant temperature while testing. Input gases to the anode and cathode manifolds excluding water were supplied by premixed gas bottles with the composition given in Table 2. Electric heating cartridges preheated the gas output from the bottles. After preheating, water to the required proportion was injected to the gas streams before entering to the gas manifolds. The acquired polarization curves for the cells with alumina-coated surfaces of the matrix and without it are depicted in Fig. 7.

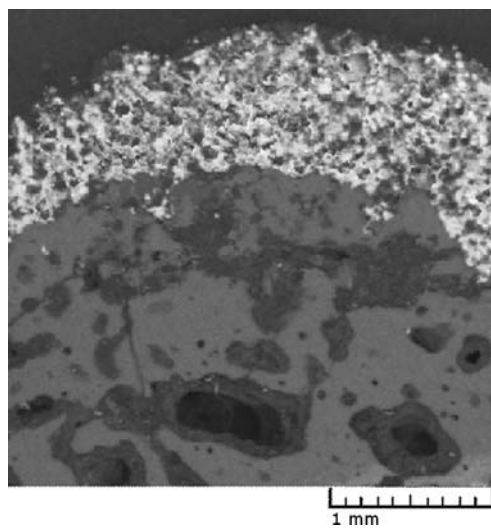
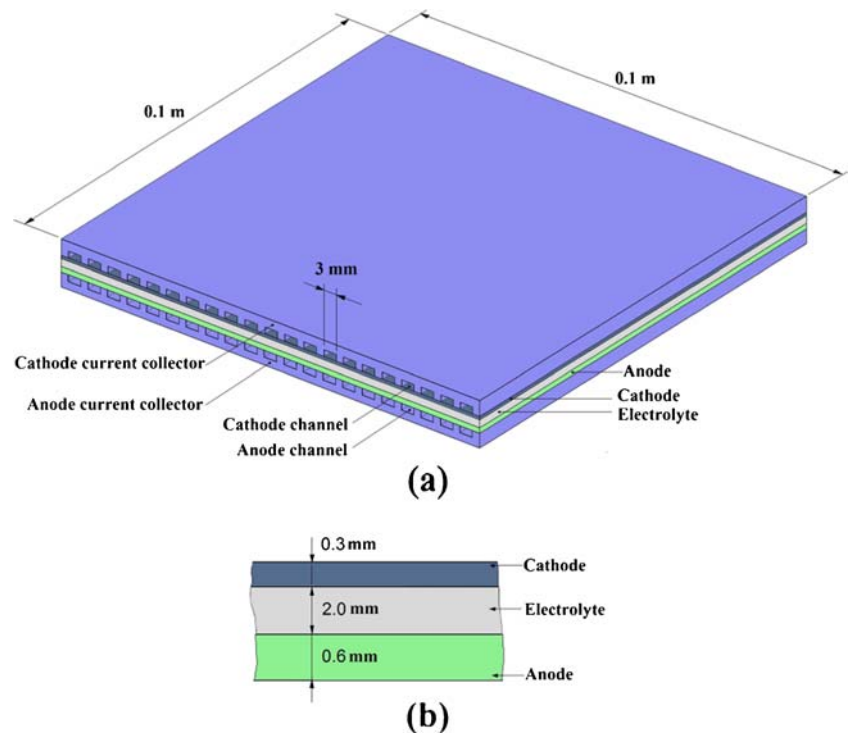


Fig. 5 Micrograph of thermal sprayed Ni anode layer

Fig. 6 a, b Geometry and dimensions of manufactured cell



Electrolyte vaporization test

The aforementioned manufacturing procedures for MCFC were applied on a matrix with described alumina slurry coating and on a matrix with similar geometry cut from insulator brick in as sawed condition. Then, the prepared cells were placed in a furnace at 650 °C for periods of 5 h, and were weighted with a precision of 0.01 g after each period. The amount of weight reduction in each period indicates the amount of carbonate salt vaporization. Figure 8 depicts the carbonate salt vaporization rate in these experiments. The amount of weight loss is higher in the sample without alumina coating at the surfaces.

SEM images of 10 samples (with alumina coating at the matrix surfaces) exposed to testing condition (650 °C) for 2 and 100 h were prepared. Typical of these images are

Table 2 Input gases constituents during the cell test

Gas constituent	Molar fraction
H ₂ in the anode input gas	0.60
CO ₂ in the anode input gas	0.15
H ₂ O in the anode input gas	0.25
O ₂ in the cathode input gas	0.08
N ₂ in the cathode input gas	0.59
CO ₂ in the cathode input gas	0.08
H ₂ O in the cathode input gas	0.25

shown in Figs. 9 and 10 for testing times of 2 and 100 h, respectively. After 2 h the large pores of the insulator were still full of the carbonate salt, whereas after 100 h that the sample was at high temperature of 650 °C, some large pores of the insulator became empty of the electrolyte. Small pores of the coated area were full of the electrolyte at both times.

Results and discussion

In Fig. 2 the section of initial matrix piece sawed from an insulator brick is depicted. Figure 4 shows the NiO cathode

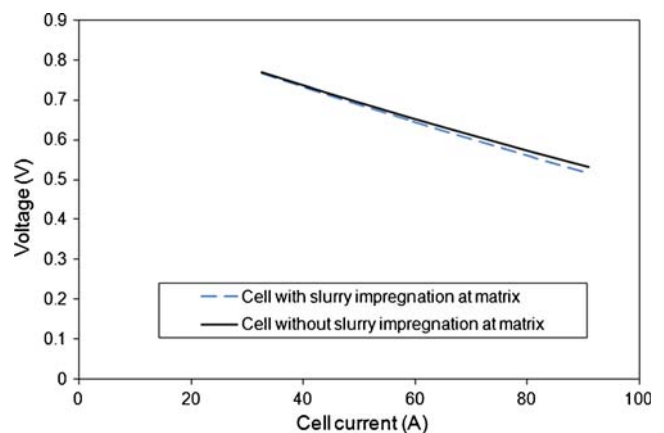


Fig. 7 Polarization curves of tested MCFCs

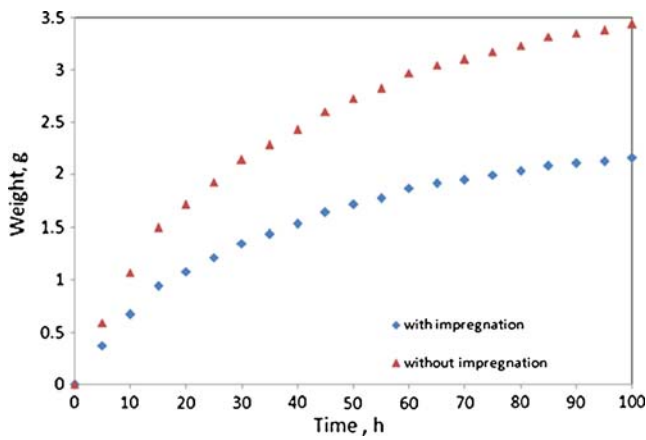


Fig. 8 Electrolyte vaporization of cells at 650 °C

layer produced on the surfaces of the matrix coated with the slurry as the substrate. The porosity of this cathode layer was measured using an image analyzing procedure to be 36% on average. The coated areas of Figs. 3 and 4 which are coated by the slurry method provide zones with low pore size to facilitate management of molten carbonate salt content. In this way, the volume of stored carbonate salt in the matrix is increased while the condition of partial filling of the electrode porosities for producing three boundary zones is readily established.

As shown in Fig. 7, the polarization curves for the two varieties of cells are very similar to each other except for a trivial difference in the slopes which can be attributed to different interface areas of liquid electrolyte and electrodes resulting in dissimilar ohmic polarizations. The alumina surface coating restricts the contact area of liquid electrolyte with the electrodes that results in higher ohmic polarization.

The results of electrolyte vaporization tests shown in Fig. 8 indicate that the cell with its matrix surfaces coated with alumina slurry has lower weight reduction when

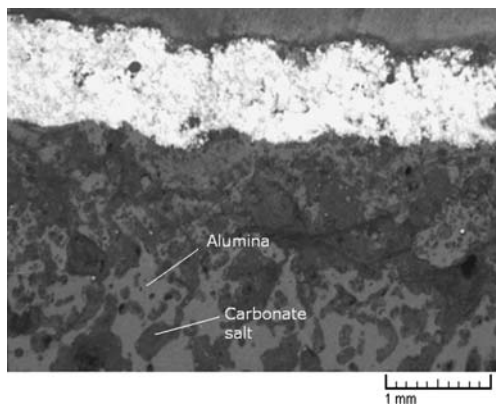


Fig. 9 Sample with alumina coating tested for 2 h

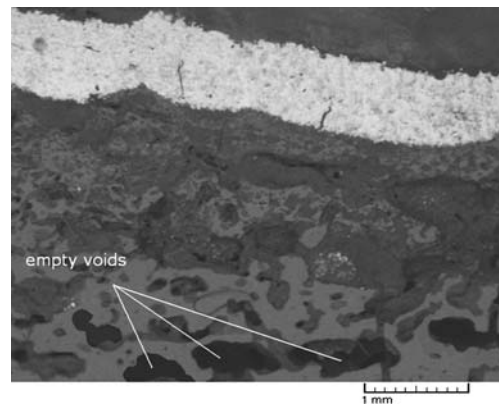


Fig. 10 Sample with alumina coating tested for 100 h

placed in the furnace at 650 °C. The percent of vaporized carbonate salt mixture relative to initial salt content in the cell without slurry coating and in the cell with all of its surfaces coated with alumina slurry are 22.9% and 14.4% for 100 h of heat treating process, respectively. The rate of electrolyte vaporization is at maximum at the initial heating periods and diminishes as heating time proceeds. The reason is that after a long period of time, the open pores at the surface of the matrix are blocked by precipitated material. This phenomenon is more probable when the open pores' size is reduced (for example by alumina slurry coating). The interesting point is that in spite of the decrease in the salt content in large pores of the insulator, small pores of the coated surface were always full of the carbonate salt due to their more surface tension effect (Figs. 9 and 10).

Conclusion

An economic manufacturing process for MCFCs presented that omitted molding stage for fabrication of the matrix and makes use of economic process of thermal spraying for deposition of the anode layer. An insulator brick with large pore size was used for producing thin matrix sheets from it through sawing process. Coating of the surfaces of these matrix sheets with alumina slurry reduced the pores size of the matrix at its interface with the electrodes which facilitated the liquid electrolyte management while preserving a larger amount of electrolyte in the porous matrix.

The application of a thin layer with low pore size produced by alumina slurry coating into the matrix also reduced the amount of liquid electrolyte vaporization during operation of the cell which can be attributed to sooner blocking of small pores comparing larger ones. However, application of the slurry coating on the matrix surfaces did not significantly increase the cell ohmic loss.

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References

1. Tomczyk P (2006) *J Power Sources* 160:858–862
2. Farooque M, Maru HC (2001) Fuel cells—the clean and efficient power generators. *IEEE Proc* 89:1819–1829
3. Fontes E, Lagergren C, Simonsson D (1993) *Electrochim Acta* 38:2669
4. Maric R, Ohara S, Fukui T, Yoshida H, Nishimura M, Inagaki T, Miura K (1999) *J Electrochem Soc* 146:2006
5. Dicks AL (2004) *Curr Opin Solid State Mater Sci* 8:379–383
6. EG&G Services, Parsons Inc. (2000) Fuel cell handbook, 5th edn. U.S. Department of Energy, Morgantown
7. Breeze P (2005) Power generation technologies. Elsevier, Amsterdam
8. Youn JY, Yoon SP, Han J, Nam SW, Lim TH, Hong SA, Lee KY (2006) *J Power Sources* 157:121–127
9. Hyun SH, Cho SC, Cho JY, Ko DK, Hong SA (2001) *J Mater Sci* 36:441–450