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Fabrication and properties of combined electrode/electrolyte tape for molten carbonate fuel cells

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A process which would simplify the fabrication procedure of a Molten Carbonate Fuel Cell (MCFC) is described. Green tapes of the combined electrode/electrolyte type were fabricated by a double doctor blade method. Then the combined tapes were burnt-out in-cell by elevating the temperature to 650° C. During the burn-out process, under stack compression (0.15 MPa), the electrolyte composites became dense ($2.24\,\mathrm{g\,cm^{-3}}$) and gas-tight. On the other hand, the anode tape and the cathode tape were sintered or *in situ* oxidized to form porous plaques. Single cells made by this process exhibited performance characteristics of 0.80 V at $150\,\mathrm{mA\,cm^{-2}}$ ($H_2/CO_2/H_2O$ 66/16/18 $U_f = 65\%$, air/CO_2 70/30 $U_0 = 61\%$). Though there remain some problems, such as thickness decrease of the tape and cross-leak during the burn-out process, this new process may be attractive for MCFCs.

1. Introduction

The Molten Carbonate Fuel Cell (MCFC) is under development as a high efficiency electricity generator. The main components of an MCFC are the anode, the cathode and the electrolyte composite. The electrolyte composite was earlier fabricated by hot pressing [1], while nowadays it is fabricated by various more economic techniques such as tape castings [2], roll millings [3], and paper-making methods [4].

By contrast the anodes, which are porous nickel plaques with porosity of 60–80%, are usually fabricated by firing nickel-based alloy powders (Ni-Cr, Ni-Al etc.) or mixed powders of nickel and refractories at 900–1000° C under a reducing atmosphere [5–7]. The cathodes are usually made by the same method as the anodes, and are then oxidized and lithiated during cell operation. From the viewpoint of large scale fabrication of MCFCs, these processes for preparing the electrodes may not be efficient compared with those for the electrolyte composite. Furthermore in those processes which treat sintered electrodes and matrix type electrolyte composites, good contact between these components is not always assured. If the processes for fabricating the electrodes and the electrolyte composite were simplified and also good contact between electrodes and electrolyte composite could be assured, then this would be an important improvement in the fabrication of MCFCs.

The aim of this study was to investigate a new process for fabricating combined electrode/electrolyte tape which does not need firing before the assembly of the cells. The binder of the combined tape would be automatically burnt-out in-cell by elevating the temperature to 650° C, and the tape would function as electrodes and electrolyte composite. In this paper, the viability of this new process is explored.

2. Experimental details

2.1. *Fabrication*

The raw material for the electrolyte tape was prepared by mixing carbonate (60 w/o, 62/38 m/o Li_2CO_3/K_2CO_3) and $LiAlO_2$ (40 w/o, Foote Mineral Co., $10\,\mathrm{m^2\,g^{-1}}$) at 650° C, then cooling and grinding to 32 mesh or finer.

Two types of nickel powder used for the anodes. One was carbonyl nickel powder (INCO type 255, $d = 2$–$3\,\mu\mathrm{m}$); the other, nickel powder coated with fine alumina powder (Degussa Aluminium Oxide C, $d = 0.02\,\mu\mathrm{m}$) to provide resistance against creep. The method of coating nickel particles with fine alumina particles has been described previously [8]. For the cathodes, nickel powder without further treatment was used. Both anode and cathode tapes contained 10 w/o of fine carbonate powder to minimize the absorption of carbonate from the electrolyte composite.

The raw materials were ball milled with solvent (ethanol/toluene = 4:6), binder (polyvinylbutylal: PVB) and plasticizer (dibutyl phalate: DBP). After the mixture had been milled for the required time, the obtained slurry was degassed in vacuum for 5 min. Then the slurry was cast into tape by the doctor blade method. The conditions for preparing the slurry were examined with respect to the milling time, the median particle size and the apparent viscosity of the slurry.

2.2. *Burn-out and cell test*

In the MCFC, the combined tape should be burnt-out in-cell during a gradual elevation of temperature to 650° C. The burn-out conditions were examined by DTA, TG and tube tests. The tube tests were conducted

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Table 1. The median particle diameter and the viscosity of the electrolyte slurry prepared with various milling time

Time (*h*)	0	2	4	8	20	48
Diameter (μm)	16	9	7.7	7.5	7.1	4.5
Viscosity ($\times$ 10^3cp)	–	–	–	2.5	4.0	5.0

by using 'U'-shaped quartz tubes set in an electric furnace. The composition of feed gas and the rate of temperature increase were changed in every test run. The cell tests were carried out with small single cells (effective area = 24.5 cm^2) supplying pseudo anode gas ($H_2/CO_2/H_2O$ 66/16/18 v/o, 60 $cm^3 min^{-1}$), and pseudo cathode gas (air/CO_2 70/30 v/o, 120 $cm^3 min^{-1}$) with a stack compression of 0.15 MPa. The porosities of the electrodes and the electrolyte composite were measured by Hg porosimetry (Micromeritic Model 9200). Carbonate contained in samples was washed out previously with acetic acid and distilled water.

3. Results and discussions

3.1. *Fabrication of the tape*

The characteristics of the electrolyte slurry affect the properties of the electrolyte tape and also affect the burn-out behaviour and cross-leak through the final electrolyte composite. So the preparation and the characterization of the electrolyte slurry are important. Table 1 shows the change of median particle size and apparent viscosity of the electrolyte slurry with milling time. The electrolyte slurry was prepared by milling a mixture of $LiAlO_2$/carbonate and solvent (52 cm^3/100 g of solid). In this step PVB and DBP were not added because PVB raises the viscosity of the slurry and lowers the efficiency of milling. To test the flow properties of the slurry, PVB and DBP (5 g each /100 g of solid) were added to the slurry and the latter milled again for 1 h. The slurry prepared by milling for 10 h contained large size particles and its flow characteristics were not suitable for the doctor blade method. The electrolyte tape made from the slurry showed low density ($\sim$1.35 $g cm^{-3}$) and poor flexibility. The slurry made by 48 h milling was also not suitable for casting because of its high viscosity. It needed additional solvent to improve the flow characteristics, and this addition of solvent lowered the density of the tape cast from the slurry.

After examination and also considering the smoothness of the tape surface, a preferred method of fabricating electrolyte tape was developed using the slurry prepared by the 48 h milling process. This consists of 2 steps: first, milling for 24 h with solvent but without PVB and DBP; second, 24 h milling with PVB and DBP.

Tape casting was successfully conducted with the slurry and then the tape was dried at 60° C for 15 min. After the tape was dried, its thickness was 0.9 mm for a 1.5 mm opening of the doctor blade, the porosity was 35 v/o and the density was about 1.5 $g cm^{-3}$. The tape showed flexibility and it was able to bend at a curvature of 40 to 50 mm radius.

Concerning the slurry for the anode and the cathode, these were successfully prepared by 1 h milling of the raw materials, that is, 100 g nickel powder, 5 g PVB, 5 g DBP, and 105 cm^3 of solvent. The electrode slurry was degassed, and then cast and dried without any problem.

The combined electrode/electrolyte tape was fabricated by the double doctor blade method. First the electrolyte tape was cast and dried, then the electrode tape was cast on top of the electrolyte tape and dried. In this work, an electrode was attached to one side only of the electrolyte tape. To assemble the cells, two types of combined anode/electrolyte and cathode/electrolyte tape were attached to each other by their electrolyte faces to become one component.

3.2. *Burn-out*

The results of DTA and TG measurements in air show that PVB and DBP begin to decompose at about 200° C and completely burn-out at 600° C. Table 2 shows the properties of electrodes and electrolyte obtained by burn-out in the tubes under various conditions. The burn-out was carried out by raising the temperature from 100° C to 650° C in 2 to 24 h.

The anode tape made from normal nickel powder was easily burnt-out and sintered, yielding a soft porous plaque under dry H_2 and under H_2/H_2O. Under N_2/H_2O, the nickel was slightly oxidized and showed weak sintering. Figure 1 presents the effect of the PVB contents on the porosity and the median pore diameter of the burnt-out anodes (non-treated nickel). These values are larger than desirable for the anodes, but it should not be difficult to optimize them by properly selecting the powder and the PVB content.

The anode tape made from alumina coated nickel powder did not show sintering when the tape was burnt-out alone. But in the case of the anode/electrolyte tape under stack compression it became a porous plaque. For the cell tests, the anode tape made from alumina coated nickel powder with 5% PVB contents was used.

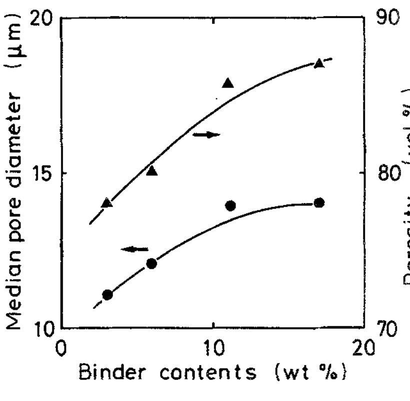

Fig. 1. The median pore diameter and the porosity of the anodes gotten from the tapes of various binder contents.

Table 2. Burn-out conditions and results

Gas	Dry H_2		$H_2 + H_2O$*		Air + CO_2		$N_2 + H_2O$	
Time (h)	2	24	2	24	2	24	2	24
Anode	S†	S	S	S	–	–	M‡	M
Electrolyte	black	gray	black	white	white	white	gray	white
Cathode	–	–	–	–	O§	O	M	M

* 60° C humidity.
** Time to elevate temperature from 100° C to 650° C.
† Sintered.
‡ Slightly oxidized, weak sintering.
§ Oxidized and lithiated.

The cathode tape was easily burnt-out under air/CO_2. It was oxidized and lithiated, and formed a black fragile porous plaque. It was the same in the case of the cathode/electrolyte tape. This is similar to the usual *in situ* cathode which is initially a strong sintered plate, but becomes fragile after *in situ* oxidation.

The burn-out of the electrolyte tape under dry hydrogen was not successful because of the carbon residue. Binder and plasticizer were successfully burnt-out under H_2/H_2O, air/CO_2 and N_2/H_2O, with small rates of increase of the temperature. The 2 h burn-out rate was not desirable, because rapid gassing made the electrolyte composite highly porous.

The electrolyte produced by burn-out in the tube tests was too porous to prevent cross-leak. Furthermore, a shrinkage of about 5% in the direction of the plane was observed after the burn-out process. These problems would be serious in the use of combined tapes for MCFCs. Table 3 and Fig. 2 show the effect of compression during the burn-out process on the porosity, the density and the thickness of the electrolyte tape. As the compression becomes larger, the porosity and the thickness become smaller. The shrinkage is also made negligibly small by the application of compression.

These results show that it is necessary to apply compression during the burn-out process. For the MCFC the usually adopted stack compression is 0.1 to 0.3 MPa; this compression would be sufficient to make the electrolyte tape gas-tight.

Though the decrease in thickness is relatively large (ex. 48% decrease for 0.1 MPa) and unavoidable, this problem may be solved by suitable cell stack design taking the thickness change into account.

Table 3. The change of density, porosity and thickness of the electrolyte burnt-out under various compression. (Burnout conditions: in air, 650° C, 24 h)

Compression (MPa)	Density ($g\,cm^{-3}$)	Porosity ($cm^3\,g^{-1}$)	Thickness (mm)
Green tape	1.48	0.228	1.20
0.00	1.93	0.098	0.84
0.01	2.18	0.034	0.74
0.05	2.23	0.027	0.72
0.10	2.24	0.022	0.70
0.15	2.24	0.018	0.69

3.3. *Cell performance*

The combined tape used in cell tests had an anode (alumina treated) and cathode layer of 1.0 mm thickness each, and two electrolyte layers of 1.8 mm. The electrodes on the wet seal area were scraped off. In the case of large size combined tape, the wet seal area should be left by limiting the casting width of the electrodes or by masking against the electrode slurry. The cell mount had a basin of 2.0 mm depth to contain the electrode and current collector. The current collectors were 1.5 mm thick, and they contained channels for gas flow. A 0.5 mm difference between the depth of basin and the total thickness of electrode and current collector provided a margin for the change in thickness of the electrodes during the burn-out process.

Single cells using combined tapes from various lots were burnt-out using the temperature patterns shown in Fig. 3, simulated anode and cathode gas, and a stack compression of 0.15 MPa. The cell voltage rapidly rose when the temperature exceeded the melting point of the carbonate (495° C), and became about 1.09 V at 650° C. The theoretical open circuit voltage (OCV) at 650° C is 1.067 V under the assumption that the shift reaction is in equilibrium [9, 12]. The difference between theoretical and experimental OCV might be caused by the partial condensation of water in the gas feeding tube.

Before the cell tests, a serious problem was expected

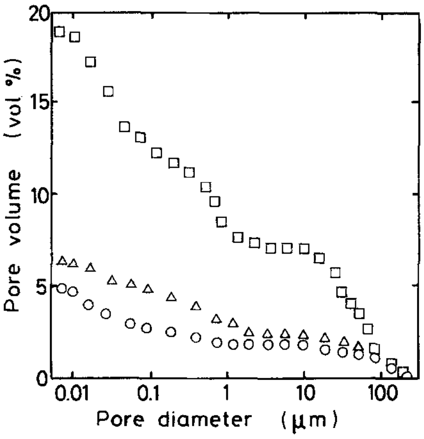

Fig. 2. Comparison of electrolyte composite pore distribution as a function of compression applied during the burn-out process. □: 0 MPa, △: 0.01 MPa, ○: 0.10 MPa.

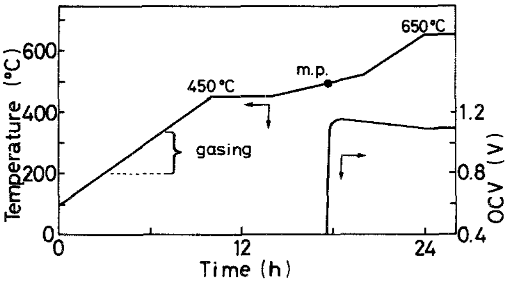

Fig. 3. The pattern of temperature for in-cell burn-out, and the change of open circuit cell voltage.

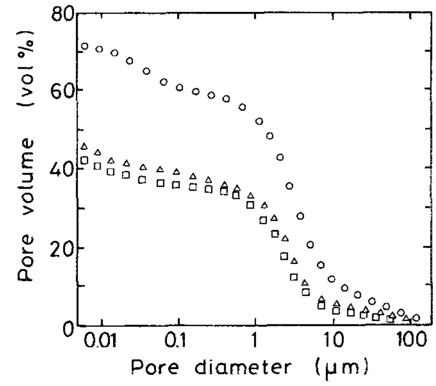

Fig. 5. The pore distribution of the anodes, after cell testing for 100 h, 1000 h and 2000 h (without electrolyte). ○: 100 h, △: 1000 h, □: 2000 h.

in which the electrolyte composite would not be gas-tight at the temperatures below 495° C. This means feed gas leaking from the wet seal, since the cross-leak of gases in the cells is unavoidable. Actually it was observed that a large part (~ 50%) of the feed gas leaked out from the wet seal area until the temperature exceeded the melting point. The cross-leak was also large and oxidation of hydrogen was expected to occur at the electrodes. Exit gas analysis showed that the anode exhaust gas contained only ~ 10–20% hydrogen.

In spite of these conditions, at temperatures over 500° C most of the cells showed normal OCV (at 500° C OCV were about 1.15 V; theoretical OCV, considering the shift reaction, is 1.096 V), and the cross-leak was about 0.5% (that is, nitrogen contained in anode exhaust). The gas permeation rate through the electrodes and electrolyte was about 4 $cm^3 atm^{-1} cm^{-2} min^{-1}$ for 0.1 atm hydrogen. This value seems to be a little large compared with those for electrolyte composites produced by other processes.

About 20% of the tested cells showed a large amount of cross-leak, and in some of these cross-leak was reduced by increasing the stack compression. When a low-density electrolyte tape is used, the frequency with large cross-leak occurred was increased. Upon inspection of these cells, small cracks or small dry areas were found in the electrolyte composite. These cracks appear to be caused by lack of stack compression in the electrode area. The small dry areas appear to be caused by the presence of a hot zone where the combustion of hydrogen occurs. These problems may become serious in the case of large scale cell stacks. The use of humidified N_2/5% H_2 gas to alleviate these problems was also examined. In-cell burn-out tests were carried out by feeding humidified N_2/5% H_2 gas to the anode chamber and humidified nitrogen to the cathode chamber. When the temperature exceeded 500° C, the gas feed was changed to simulated MCFC feed gases. By this method the fraction of large cross-leak occurrences decreased to about 10%.

After the burn-out process, the test cells having low cross-leak (~ 0.3%) were kept on open circuit for two days to ensure burn-out effectiveness and lithiation of the cathode. Fig. 4 shows a typical current-voltage characteristic for a single cell using combined electrode/electrolyte tape. The performance was comparable to that of a cell using the usual sintered electrode [9]. Fig. 4 also shows that the decay in cell performance was about 80 mV (at 150 mA cm^{-2}) after operation for 860 h.

Figs 5 and 6 show the distribution of pore size for anode and cathode after cell testing for 100 h, 1000 h and 2000 h. These show a large decrease in porosity and median pore size of electrodes. The in-cell burn-out of the anode under relatively low temperatures results in loose sintering. The sintering process of the anode should occur during the cell operation, and it may need several hundred hours

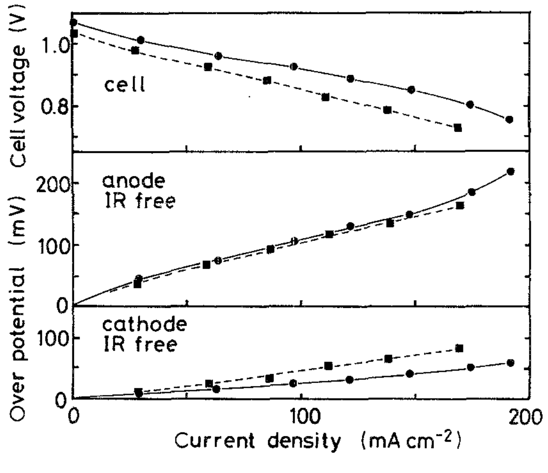

Fig. 4. The discharge curves of the single cell using the electrode/electrolyte combined tape. ●: 100 h, ■: 860 h.

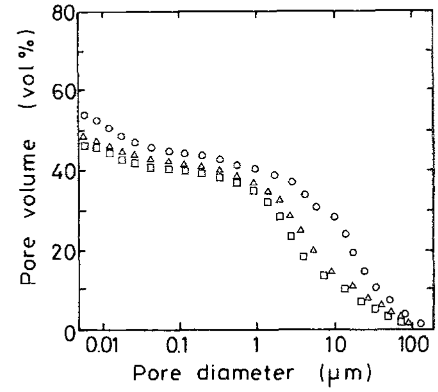

Fig. 6. The pore distribution of the cathodes, after cell testing for 100 h, 1000 h and 2000 h (without electrolyte). ○: 100 h, △: 1000 h, □: 2000 h.

before the sintering speed becomes small. In fact, in the initial 1000 h a large decrease in the porosity and the mean pore size was observed; only after 1000 h did the change in pore size distribution became small. The problem of large changes in microstructure caused by sintering or creep may be restrained by using anti-creep materials such as Ni-Al or metal plated ceramics.

Concerning the cathode, the porosity after 100 h was rather small compared with the anode. This difference would be caused by skeletal expansion along with the oxidation of nickel. After 1000 h, however, the mean pore size decreased. This change would depend upon the fragility of the in-cell oxidized tape cathode and the stack compression. The small size pores tend to suck up the electrolyte, hence both anode and cathode would have sucked up electrolyte from the electrolyte composite. Usually the cathode is highly sensitive to the electrolyte content [10], so the excess electrolyte in the cathode should have caused a large decay in cathode performance.

The other causes of the decay in cell performance would be the increasing *IR* loss of the electrolyte composite and the cross-leak. The change in electrolyte distribution and the progress of corrosion would have made the electrolyte composite dry [11]. Actually, the contents of the electrolyte composite after a 2000 h cell test was decreased to 75% of the initial bulk. The dried electrolyte composite increases not only the *IR* loss but also the cross-leak ($\sim 2\%$). The decrease in OCV shows the effect of increasing cross-leak.

Inspection of the cells after a 2000 h test showed that electrodes and electrolyte composite were tightly bonded. Generally, good contact of electrodes and electrolyte composite is important for efficient cell peformances. From this point of view, a combined electrode/electrolyte tape is desirable because its initial bonding ensures perfect contact of electrodes and electrolyte. Such good contact characteristics may have compensated for the possible disadvantages of electrodes caused by the in-cell burn-out process.

The principle problem of this process is the decrease in thickness of the tape during the burn-out process. Therefore, accurate prediction of the change in thickness is important for the design of stacks. Further work is needed to make the electrolyte tape cross-leak free and to decrease the change in microstructure of electrodes.

4. Conclusion

Combined electrode/electrolyte tapes may be fabricated by the double doctor-blade technique and such tapes would be conveniently applied in an MCFC assembly by means of in-cell burn-out. MCFC cells, containing components made by this tape casting and burn-out procedure, showed performances comparable to those of cell components produced by the usual processes. Though some problems remain, such as change of thickness and gas cross-leak, the combined tape process may be more effective than existing procedures for mass production and scale-up of MCFCs.

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