The Korean Journal of Ceramics, **2** [3] 142-146 (1996)

Effect of Reinforcing Materials on Properties of Molten Carbonate Fuel Cell Matrices

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(Received September 2, 1996)

The molten carbonate fuel cell matrices, which are usually made of high surface area, fine particle size γ-$LiAlO_2$, are reinforced with coarse particles of the same material and alumina fibers. And the effects of reinforcing materials on pore characteristics, sintering properties and mechanical properties of the matrices are examined. Among the matrices examined, the highest mechanical reinforcement has been achieved in the one containing 10 wt.% coarse particles and 20 wt.% alumina fibers.

Key words : γ-$LiAlO_2$, Alumina fiber, Porosity, Pore, Mechanical strength

I. Introduction

The MCFC(Molten Carbonate Fuel Cell) is now under active development as an electricity generator of high efficiency. The main components of an MCFC are the anode, the cathode and the electrolyte matrix, a combination of electrolyte plus matrix. Since the carbonate electrolyte is in the liquid state at the MCFC operation temperature, it is the practice to contain the electrolyte in a presintered inert porous matrix. Therefore the matrix must have porosity of 50-70% for electrolyte retention, pore sizes much less than those of electrodes, usually in the range of 0.1-0.5 μm, to prevent flooding, and such thin thickness to reduce IR-drop to a minimum.[1)]

Lithium aluminate($LiAlO_2$) is known to be the most adequate material for matrix because of its chemical stability in the commonly-used Li/K carbonate electrolyte. Lithium aluminate has three polymorphic forms among which gamma(γ) is the most stable one at the MCFC operation conditions. Commercial γ-$LiAlO_2$ powders are for sale in two types, one of high surface area(HSA) and the other of low surface area(LSA), and the former, specifically the one with surface area of 10 m^2/g, is usually used for the fabrication of matrices.[2)] But the matrices made only of HSA powders are mechanically weak and vulnerable to crack formation and propagation. Therefore LSA powders as well as fibers either of lithium aluminate[2)] or of alumina are used as reinforcing materials. It has been reported[2)] that coarse particles of LSA powders limit crack propagation and fibers prevent crack formation.

Tape casting is a method most frequently adopted for the fabrication of matrices.[3)] In tape casting a slurry is made by mixing lithium aluminate powders with a binder in an organic solvent and the viscous slurry is then allowed to pass under a knife-edge so that a tape is cast. The viscosity of the slurry is very important in tape casting because it seems to be related with crack formation during subsequent drying and sintering of tapes. And it depends strongly on the amount of binder added to the slurry.In this study MCFC matrices were fabricated by tape casting mainly with HSA lithium aluminate powders. Various amounts of LSA lithium aluminate powders and alumina fibers were added as reinforcing materials and their effects on pore characteristics, sintering properties and mechanical properties of the matrices were examined. Also the rheological behavior of the slurries was checked and efforts were made on searching for optimal binder contents to yield proper slurry viscosity for tape casting.

II. Experimental Procedure

Gamma lithium aluminate powders of high surface area(HSA-10) and those of low surface area(LSA-50) were purchased from Cyprus Foote Mineral company. The surface areas of HSA-10 and LSA-50 were 10 m^2/g and less than 0.1 m^2/g, respectively. And the average particle sizes of HSA-10 and LSA-50 were 2 μm and 50 μm, respectively. Alumina fibers of 3 μm diameter with an aspect ratio of 10-20 were purchased from Zircar company.

A flow diagram for the complete process of tape casting is shown in Fig. 1. HSA-10, LSA-50 and alumina fibers together with corn oil as a deflocculant and toluene/ethanol mixture as a solvent were initially ball-milled for 24 hours in a nylon jar. The amount of LSA-50 or alumina fibers was varied up to 30 wt.% of the ceramic materials. After a short stop for the addition of PVB (polyvinyl butyral) as a binder and DBP(dibutyl phthalate) as a plasticizer, additional ball milling for 48 hours followed and finally a viscous slurry was ready for tape casting. PVB binder used in this experiment was BUTVAR-98 from Monsanto company and its amount was varied from 8 to 30 wt.% of the ceramic materials.

Immediately before tape casting, viscosity of the slurry was measured at a fixed shear rate of 159.8 sec^{-1} using a concentric cylinder viscometer (VT-501, Haake Co.). But, for the viscosity measurements to get informations on the rheological behavior of the slurries, the shear rate was changed from 4.45 to 444.6 sec^{-1}. This type of measurement was made on one slurry of choice containing 30 wt.% LSA-50 and 10 wt.% alumina fibers.

Casting was performed using a laboratory tape casting unit, usually called a doctor blading machine. In this machine a slurry, fed into a hopper, was allowed through two consecutive openings under two 20 cm-wide blades located in sequence and cast onto a mylar film moving at a constant speed of 1 cm/s. The cast tape was dried on the film for approximately 12 hours, removed from the film, cut into proper sizes, and sintered at a temperature in the range of 1000-1300°C for various times ranging from 1 hour to 48 hours.

The porosities of the sintered matrices were evaluated using ASTM B328 procedure which makes use of the Archimedes' principle. And mercury porosimeter (AUTOPORE II 9220, Micromeritics) was used to measure the pore distributions of the matrices.

For mechanical strength measurements, 3-point bend tests4) were performed at a crosshead speed of 0.1 mm/min on matrices prepared in a rectangular shape of 4 mm × 42 mm size. A universal testing machine (INSTRON IV) was used for the tests and MOR (modulus of rupture) was estimated from the values of applied load at fracture and specimen dimensions.

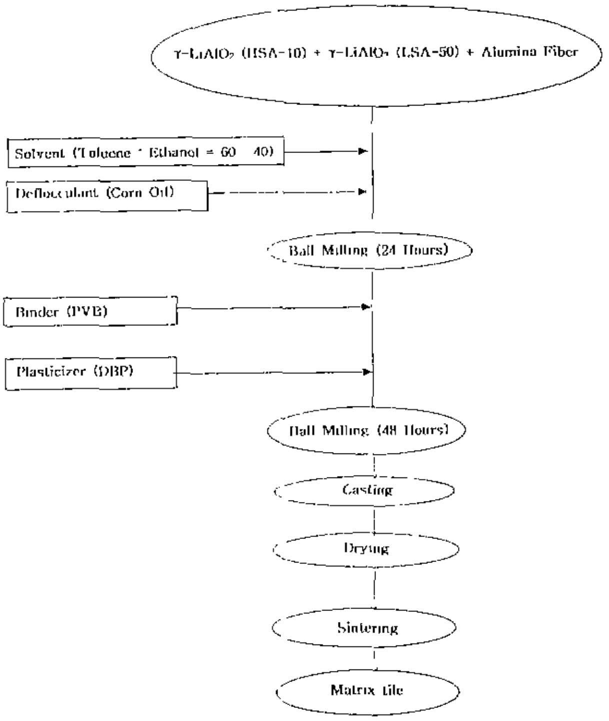

Fig. 1. Process of preparing electrolyte matrix for MCFC.

III. Result and Discussion

The pore distribution of a tape-cast matrix depends on the degree of dispersion of powder particles in the slurry and their structural stability, which are conjectured from the rheological behavior of the slurry. If colloid instability like flocculation or sedimentation occurs during casting, it is hard to fabricate matrices with fine and uniform pore distributions. The rheological behavior of the slurry containing HSA-10 only was checked previously in our laboratory[5] and turned out to be pseudo-plastic. And we have a belief based on our laboratory experiences that the pseudo-plastic behavior of slurries is adequate for tape casting

So it had to be checked first whether the addition of reinforcing materials changed the rheological behavior of the slurry. Typical rheological behavior of the slurries prepared in this study is as shown in Fig. 2 where the viscosity is plotted against the shear rate for the one containing 30 wt.% LSA-50 and 10 wt.% alumina fibers. Initially the viscosity has some high value of 10 Pas, drops rapidly with increasing shear rate, and converges to a constant value of ~4 Pas. This type of trend is known to be pseudo-plastic. Accordingly it can be assured that the reinforcing materials don't seem to change the rheological behavior of the slurries.

The viscosity of the slurry depends mainly on the binder contents in it and, as mentioned before, is related with crack formation during drying and sintering after tape casting. Therefore optimal amount of binder has to be searched. Fig. 3 shows the viscosity of the slurries containing 10 wt.% LSA-50 and 10 wt.% alumina fibers as a function of binder contents. As can be seen, the viscosity increases exponentially with increasing binder contents. Careful examinations of the matrices produced with different amounts of binder leaded us to a conclusion

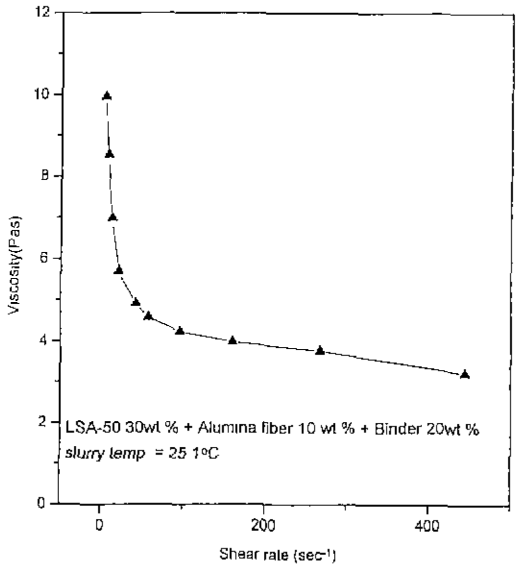

Fig. 2. Viscosity plotted against shear rate for a slurry prepared for tape casting of an MCFC matrix.

that the best quality matrix could be obtained at a viscosity of ~2Pas. According to the curve in Fig. 3, this corresponds to a binder amount of 20 wt.%.

It can be easily expected that the matrices sintered at higher temperatures have lower porosities because of the faster rate of sintering and grain growth. In Fig. 4 the variation of porosity with temperature is shown for matrices containing three different amounts of reinforcing materials, namely, none, 10 wt.% LSA-50+10 wt.% alumina fibers, and 10 wt.% LSA-50+20 wt.% alumina fibers. All three curves show the expected trend, but the decreasing rate is much faster in the first than in the last two. Similar trend can also be noticed in Fig. 5 which shows the variation of porosity with time for the above three compositions. The porosity decreases with increaing sintering time in all three cases, but the decreasing rate is faster in the case with no reinforcing materials than in the cases with them. So it can be concluded that the reinforcing materials somehow suppress sintering and grain growth of particles.

It should be noted in both Figs. 4 and 5 that the matrices containing 20 wt.% alumina fibers have higher porosities than those with 10 wt.%. This made us think that the fibers might play a role of increasing porosities. To see if this is the case we compared porosities of matrices containing different amounts of reinforcing materials as in Fig. 6. But, as you can see, no such trend

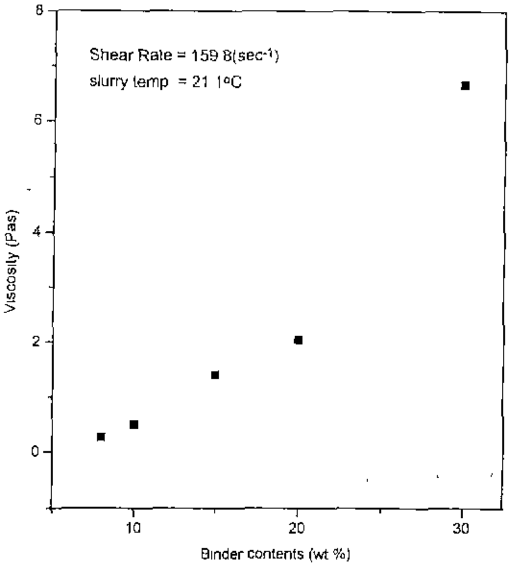

Fig. 3. Viscosity plotted against binder contents for the slurries containing 10 wt.% LSA-50 and 10 wt.% alumina fibers.

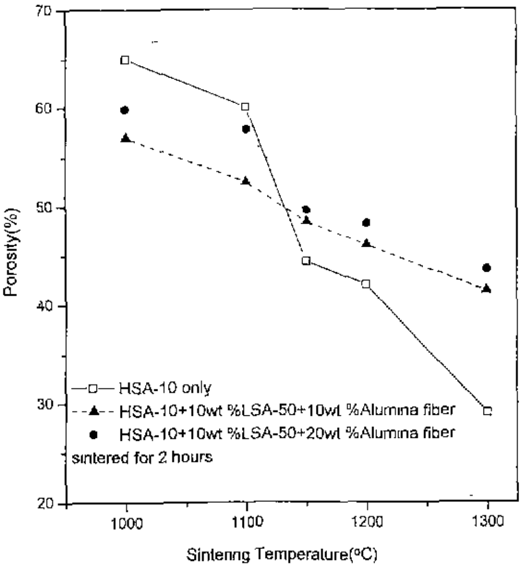

Fig. 4. Variation of porosity with sintering temperature for matrices containing different amounts of reinforcing materials.

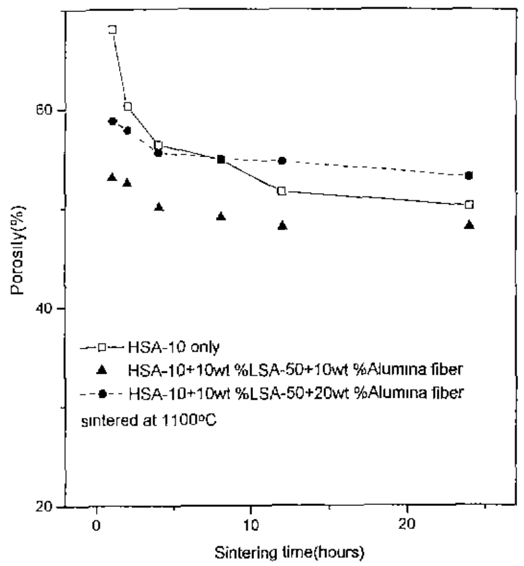

Fig. 5. Variation of porosity with sintering time for matrices containing different amounts of reinforcing materials.

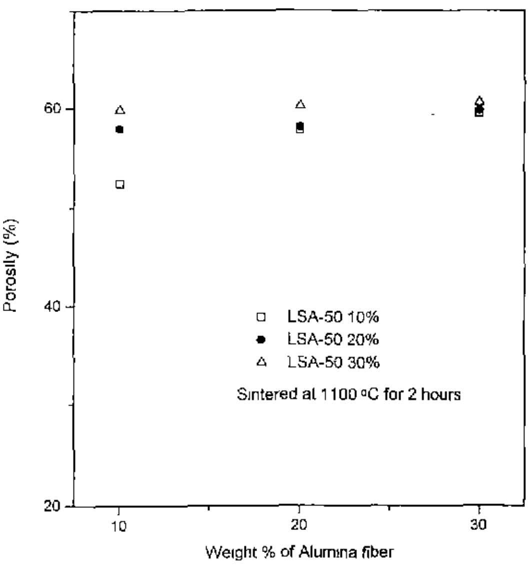

Fig. 6. Porosities of matrices plotted as a function of amounts of reinforcing materials.

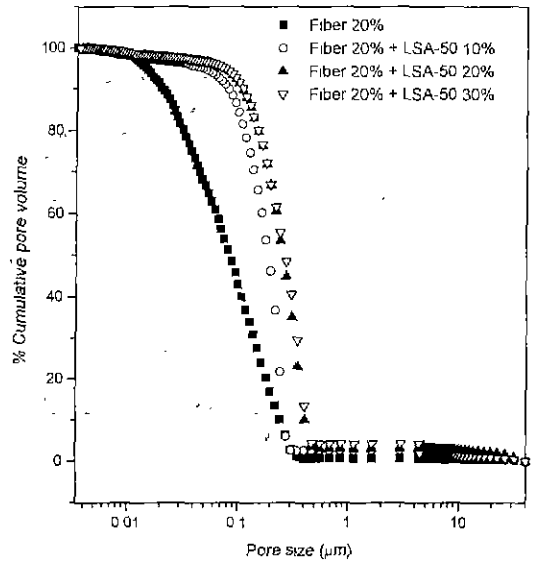

Fig. 7. Pore distribution of matrices containing 20 wt.% alumina fibers and various amounts of LSA-50.

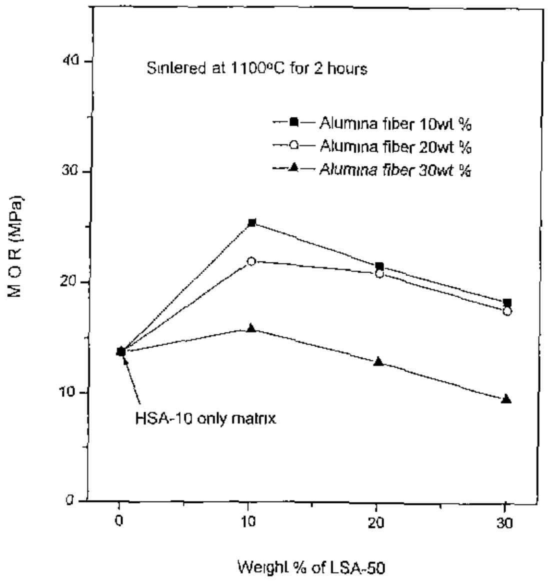

Fig. 8. Moduli of rupture of matrices plotted as a function of amounts of reinforcing materials.

can be found except the above-mentioned case.

The mean pore size as well as the pore distribution of the matrices are affected a lot by the addition of coarse particles of lithium aluminate as can be seen in Fig. 7. However, fibers didn't make noticeable changes in the pore distribution of the matrices and the pore distribution curve for the matrix containing 20 wt.% fibers almost fitted on the one with no additives. This is the reason why the latter is not shown in the figure. According to the figure the coarse particles definitely have the effect of making pore distribution sharper and mean pore size larger but still in the range of acceptable use. In Fig. 8 the mechanical strengths of matrices containing different amounts of reinforcing materials are compared in terms of MOR's. Generally the addition of reinforcing materials increases MOR. The effect is the greatest in the matrix containing 10 wt.% of both reinforcing materials and the second greatest in the one containing 10wt.% LSA-50 and 20 wt.% alumina fibers. For example MOR of 25.4 MPa for the former and 21.7 MPa for the latter can be compared with 13.8 MPa for the one with no reinforcing material. It can be also noticed in the figure that too much addition would rather decrease MOR.

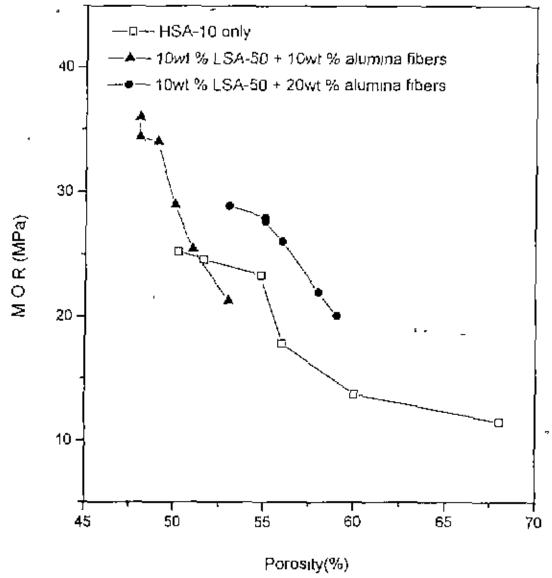

Fig. 9. Moduli of rupture of matrices containing three different amounts of reinforcing materials plotted as a function of their porosities.

In the above comparison, however, the porosities of matrices were not taken into account. Since we realized during data analysis that MOR was a very sensitive function of porosity, we had to devise other ways of comparison which would take the porosities of matrices into account. And we decided to plot MOR's of the matrices against their porosities as shown in Fig. 9. Here we can see clearly that the increase in MOR for the matrix containing 10 wt.% LSA-50 and 10 wt.% alumina fibers is due to the decrease in its porosity but actual strengthening is achieved in the case of the matrix containing 10 wt % LSA-50 and 20 wt.% alumina fibers.

IV. Conclusions

In this study, matrices for MCFC were fabricated by tape casting from high surface area γ-$LiAlO_2$ powders with coarse particles of the same material and alumina fibers as reinforcing materials And pore characteristics, sintering properties and mechanical properties of reinforced matrices were examined. The following conclusions were made in this study.

1. The rheological behavior of the slurries with reinforcing materials was pseudo-plastic.

2. The proper viscosity of the slurry for tape casting was about 2Pas and this corresponded to the binder contents 20 wt.%.

3. Coarse particle of γ-$LiAlO_2$ did have the effect on making pore distribution sharper and mean pore size larger whereas alumina fibers didn't.

4. The reinforcing materials suppressed sintering and grain growth of the matrices.

5. The highest mechanical reinforcement was achieved in the matrix containing 10 wt.% coarse particles of γ-$LiAlO_2$ and 20 wt.% alumina fibers.

Acknowledgment

This work was supported by KOSEF under Contract no. 94-0502-09-01-3.

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