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Fabrication of porous components for molten carbonate fuel cell

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Abstract

The development of porous anode, cathode and electrolyte matrix for molten carbonate fuel cell at Tata Energy Research Institute (TERI), as part of our ongoing fuel cell stack development program, is described. The final characteristics of the electrodes and matrix prepared by tape casting and sintering were found to be influenced by the processing conditions. The required properties for the anode and cathode could be achieved by controlling the sintering and slurry preparation conditions. After cell testing, anode underwent reduction in porosity. The cathode showed development of small pores as well as reduction in porosity after cell test. The matrix characteristics were a function of the slurry composition. The tapes with higher ceramic content showed the requisite porosity and pore size distribution.
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1. Introduction

Fuel cell is an efficient and environmentally friendly power generating device, which converts the oxidation energy of a fuel into electricity and heat via an electrochemical reaction. A single cell typically consists of two electrodes separated by an electrolyte. At the anode, the hydrogen fuel is converted to hydrogen ion thereby releasing an electron. The hydrogen ion moves through the electrolyte to the cathode while the electron is tapped through an external load. At the cathode, oxygen, hydrogen ion and electron combine to form water. Several cells are stacked up in series to obtain the desired power output.

Molten carbonate fuel cell (MCFC) is a high temperature fuel cell with an operating temperature of 650 °C. The state of the art anode is comprised of Ni reinforced with Cr, Al or their oxides, having a porosity of 50–70% and a median pore diameter of 3–6 microns [1]. The reinforcement of Cr, Al, or their oxides is added to the anode to reduce sintering and creep at the cell operating temperature, which can cause reduction as well as rearrangement of the pores. The starting material for the cathode is sintered porous nickel which typically has a porosity of 70–80% and a median pore size of 7–12 microns [1]. In the presence of electrolyte and oxidizing atmosphere, lithiated nickel oxide is formed. The cathode can be formed in situ inside the cell or externally. During lithiation and oxidation, the microstructure changes to form agglomerates of NiO particles containing micropores between individual particles and macropores between the agglomerates. This leads to a bimodal pore size distribution with a median pore size of 5–7 microns.

The electrolyte matrix is comprised of the molten carbonate held between the fine pores of the inert support material to form a paste like structure at 650 °C. The typical composition of the electrolyte is a 62 mol% Li_2CO_3 and 38 mol% K_2CO_3 eutectic [1] and the matrix support material is γ-lithium aluminate.

This technology is not yet commercialised; a few demonstrations are taking place in North America, Europe and Japan. The required component characteristics have been identified [1], however, not much information has been published about the processing details. In India, MCFC development was initiated only less than a decade ago. In this paper, the development of porous components at Tata Energy Research Institute (TERI) is described. The processing of porous anode, cathode

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and lithium aluminate matrix to obtain optimum characteristics and their change in properties due to cell testing are discussed. The emphasis is on the porosity and pore size distribution since they play a key role in cell performance. This work is part of our ongoing program on developing a kW level fuel cell stack.

2. Experimental procedure

2.1. Component fabrication

The starting powder used for the anode and cathode was carbonyl nickel powder (type 255 from INCO, UK). The characteristics of the powder are shown in Table 1(a). The nickel powder was mixed with suitable solvents, binder and plasticizer to form a slurry with appropriate properties for tape casting. Several trials were conducted to select the appropriate compound and amount for the solvent, binder and plasticizer. The solvent selected was a mixture of water, methanol and isopropyl alcohol; methyl cellulose was used as the binder and glycerol was used as plasticizer. The binder, plasticizer and nickel powder ratio was such that nickel amount was in the range 67–57 wt.%. The slurry was prepared by mixing the additives in the solvent using a hand blender followed by addition of Ni powder. The slurry was then ball milled for different durations using a centrifugal ball mill (model S1 from F. Kurt Retsch GmbH, Germany). In some electrodes, aluminium was incorporated during ball milling. The slurry was tape cast using a tape casting machine (A.J. Carsten, Canada) and a doctor blade.

The green tape was sintered in a programmable, controlled atmosphere, high temperature furnace. Using a PID controller, the heating rate, sintering temperature and sintering time were varied to obtain the required porosity. The heating profile contained hold times at lower temperature to allow burn out of the organic materials such as remaining solvents, binder and plasticizer. The sintering was done in an atmosphere of nitrogen in the temperature range 800–900 °C.

The matrix was made with γ lithium aluminate. The characteristics of the starting γ lithium aluminate powder (from Cyprus Foote Mineral Company, USA) are shown in Table 1(b). The matrix was prepared by tape casting. Since the matrix was being used in the green form in close contact with hygroscopic carbonate electrolyte, a non-aqueous slurry was developed for tape casting.

Due to the high surface area of γ lithium aluminate powder, the slurry formulation involved a lot of trials. The binders chosen were ethyl cellulose and poly vinyl butyral due to their ability to dissolve in non aqueous solvents. These binders were tried in combination with different plasticizers and solvents to obtain a green tape with suitable appearance, ease of removal from substrate, strength and flexibility. Based on the trials, polyvinyl butyral was selected as binder and poly ethylene glycol as plasticizer. The slurry was prepared by ball milling for 1 h and subsequently the green tape was prepared by tape casting.

Table 1
Characteristics of starting powders

(a) Nickel powder	
Purity	99.5%
Powder shape	Chain
Chain cross sectional dimension	3 microns
Chain length	20 microns
Surface area	0.6 sq.m/g
Density	8.9 g/cc

(b) Lithium aluminate powder	
γ Lithium aluminate content	>99.5%
α Lithium aluminate content	<0.5%
Surface area	9–11 sq.m/gm
Particle size	>97%−325 mesh
Average particle size	2 microns

2.2. Characterization

The porosity and pore size distribution of the electrode and matrix were determined using a mercury porosimeter (Poresizer 9320, Micromeritics, USA). The anode and cathode were analysed after sintering, after cell testing with electrolyte present and after cell testing with electrolyte removed. The electrolyte was removed by leaching in equivolumetric mixture of acetic acid and acetic anhydride. The details of the cell testing are described elsewhere [2]. To examine the change during lithiation and oxidation of cathode, small pieces of known weight and dimensions were subjected to out of cell oxidation by heating to 650 °C in air with different amounts of carbonate electrolyte on top. These pieces were further analysed to determine change in weight, volume and the pore distribution. Similarly, in case of the matrix, pieces of known weight and volume from the green tape were heated to 650 °C in air with different amounts of carbonate electrolyte on top. Subsequently, the weight loss, shrinkage and pore characteristics were determined.

3. Results and discussions

3.1. Anode

The porosity and pore size distribution of the sintered electrode was found to be a function of sintering conditions and slurry preparation conditions. The electrodes

Table 2
Densities of sintered electrode with and without Al addition

	Electrode without Al	Electrode with Al
Bulk density	2.67 g/cc	2.02 g/cc
Porosity	69 vol.%	77 vol.%

sintered for different time periods at 900 °C showed increasing density with increasing time as expected; the reduction in volume of the sample also increased correspondingly. The incorporation of aluminium also influenced the sintered density. The density and porosity of samples sintered with and without aluminium addition under same sintering conditions in Table 2 shows that there is reduction in extent of sintering due to presence of aluminium. The milling time of the slurry had a considerable effect on the pore size distribution. With increasing milling time, the pore size became smaller. The pore size distribution of samples milled for 1 and 3 h in Fig. 1 shows this effect.

Based on these observations, slurry preparation with aluminium incorporation and 3 h ball milling was selected; sintering was carried out at 900 °C for 30 min. The anode so obtained had a porosity of 66 vol.% and median pore diameter of 5.81 microns.

Fig. 2(a) and (b) show the change in porosity and pore size distribution during cell testing, with electrolyte loading of 140 and 190%, respectively, where 100% loading corresponds to volume required to fill all the pores of the matrix. A loading between 160 and 290% is considered optimum [3]. In the sample with 140% loading [Fig. 2(a)], the electrode after test with electrolyte shows flattening of the curve at ~4 μm indicating loss of pores in the 2–4 μm range compared to the original electrode. This is due to filling of the fine pores with electrolyte and the overall porosity decreases to 24 vol.%. On removing the electrolyte, some of the porosity as well as fine pores are recovered. In the second case [Fig. 2(b)], there is reduction of pores in all the size ranges along with reduction in porosity which could be due to filling of larger pores as well with increase in electrolyte content. After leaching, porosity is recovered to a lesser extent with decrease in both large and small pores.

From the earlier observations, it appears that the porosity is not entirely recovered after removing the electrolyte and the pore amount and size filled by the electrolyte is a function of the electrolyte amount. A similar decrease in pore volume after cell testing has been reported though to a much smaller extent (11% decrease) than in this case (44–55% decrease) [4]. The loss in porosity could be due to sintering during cell operation, incomplete leaching or some oxidation of nickel to nickel oxide. If the porosity reduction were due to sintering or incomplete leaching, it would be expected that there would be a preferential decrease in the smaller pores. However, the decrease is observed in all the pores which could be due to contribution from all these factors.

Though the starting anode could be obtained with the requisite properties, cell tests reveal loss in porosity indicating the need for further improvement in sintering resistance.

3.2. Cathode

The required pore size distribution for the cathode was obtained without ball milling the slurry, since ball milling led to a lower than optimum pore diameter. Sintering was carried out at 850 °C for 5 min. The cathode so obtained had a porosity of 81 vol.% and a median pore diameter of 11.42 microns.

The change in characteristics during out of cell oxidation and lithiation of cathode with different carbonate

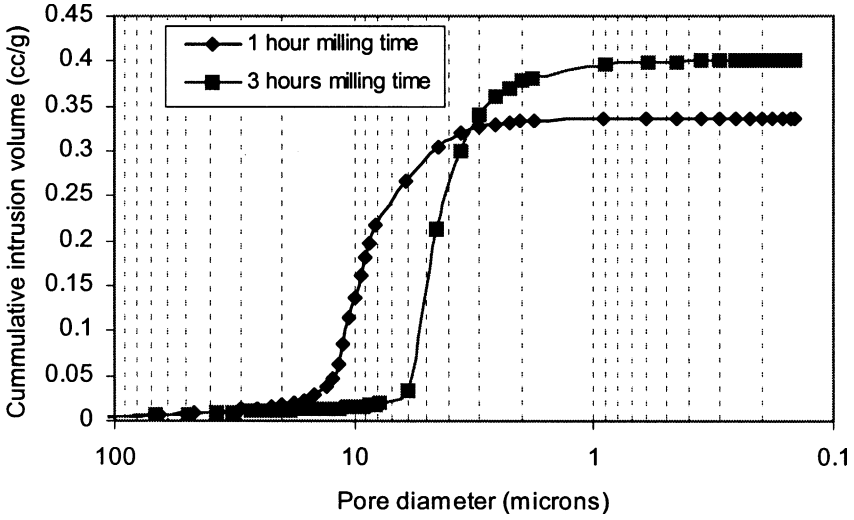

Fig. 1. Pore distribution of two electrodes milled for different time periods.

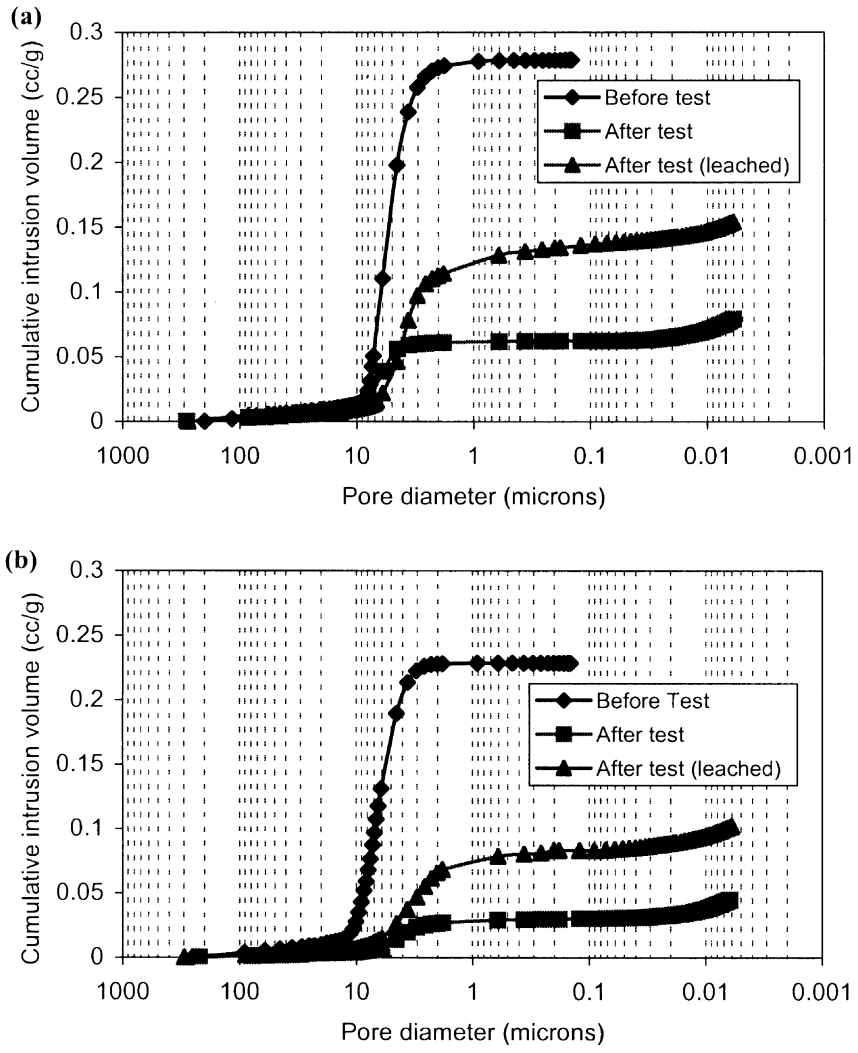

Fig. 2. Pore size distribution of anode after cell tests (a) 140% electrolyte loading (b) 190% electrolyte loading.

electrolyte loading is shown in Fig. 3. It can be observed that the oxidized cathode shows an increase in smaller diameter pores (1–4 μm) and a reduction in porosity compared to the original nitrogen sintered electrode. The shift to smaller pore diameter is greater with increasing electrolyte content; samples with 33 and 66 wt.% electrolyte show bimodal pore distribution. This is due to the formation of agglomerates of NiO particles as a result of lithiation and oxidation [5,6]. The change in porosity and pore size distribution after cell tests with carbonate electrolyte loading of 140 and 190% are shown in Fig. 4(a), and (b). The sample with 140% loading [Fig. 4(a)] shows a reduction of porosity as well loss of small pores in the range 3–6 microns. This is due to filling of these pores with electrolyte. Upon leaching, the porosity increases and the presence of pores smaller than those in the starting electrode can be observed. A similar shift to smaller pore diameter in used cathode has been reported and attributed to in situ oxidation [4]. In the sample with higher electrolyte loading, there is significant loss of porosity and loss of pores in all the size ranges. The electrolyte in case of the cell test with higher electrolyte loading appears to have preferentially filled the pores of the cathode compared to the anode [Fig. 2(b)]. Such a behaviour is expected since nickel oxide is present in the cathode which improves the electrolyte wetting. There is no significant recovery of pores due to leaching. This is partly because the electrode after leaching was very brittle and crumbled.

The out of cell tests and cell tests reveal an overall shift to smaller pore diameter and reduction in porosity due to in situ lithiation and oxidation [5,6]; however the formation of bimodal structure as expected is not very pronounced.

3.3. Matrix

During the trials to obtain appropriate slurry formulation, compositions with different ceramic content were characterised after burning out the binders at 650 °C. Fig. 5 shows the density and weight loss during heat treatment as a function of ceramic content. The

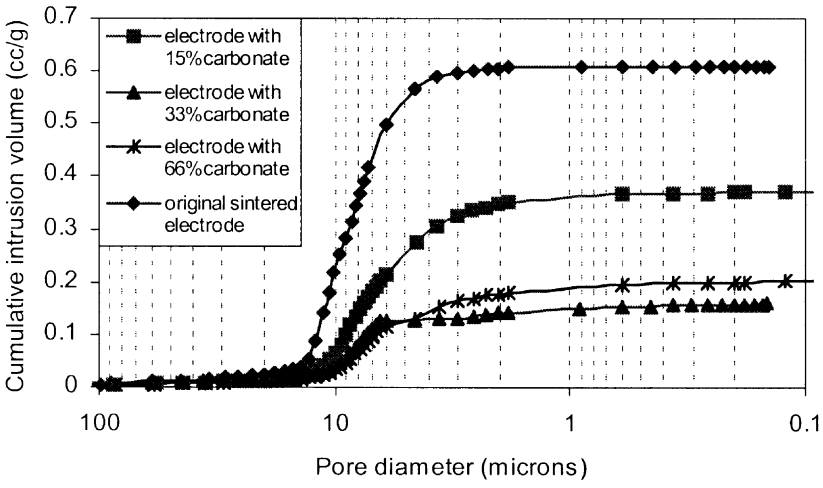

Fig. 3. Pore size distribution of cathode after out of cell oxidation with different carbonate electrolyte.

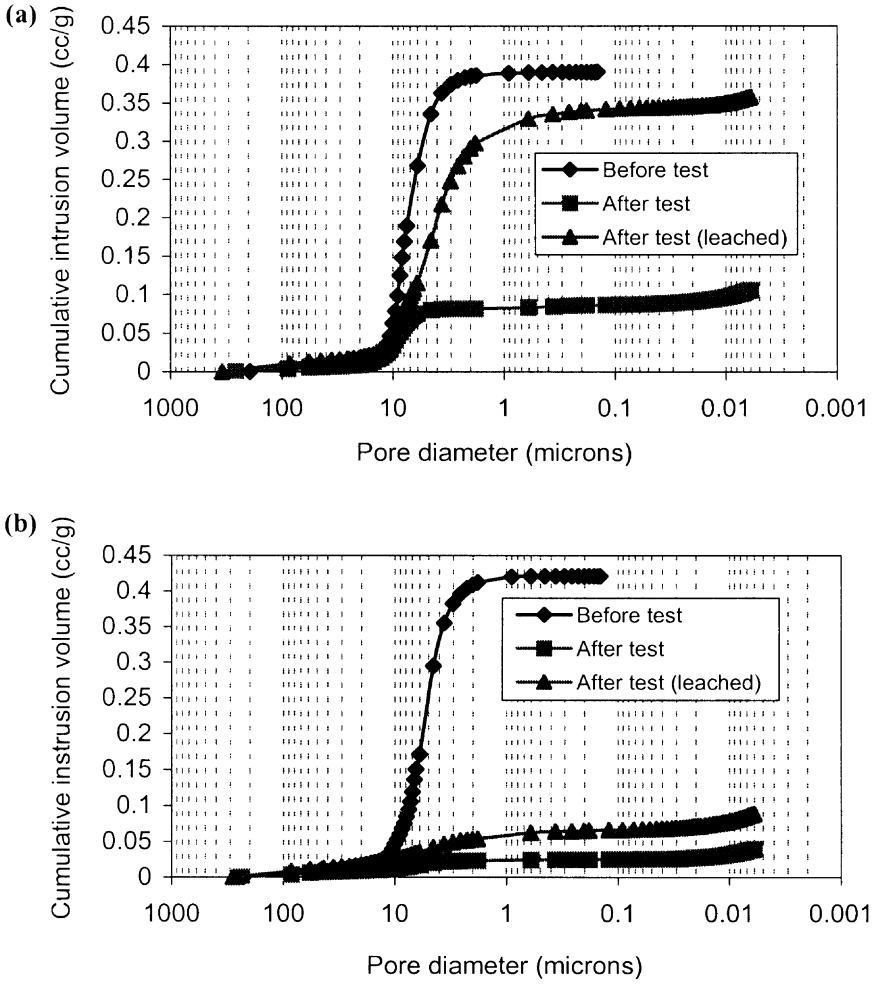

Fig. 4. Pore size distribution of cathode after cell tests (a) 140% electrolyte loading (b) 190% electrolyte loading.

final density shows an increasing trend with increasing ceramic content. This is expected since the particles would be closer packed with increasing solid content in the slurry. The weight loss also shows a corresponding decrease with increasing ceramic content.

Fig. 6 shows the pore size distribution of sample with 54, 42 and 42 wt.% ceramic heated to 650 °C with 10 wt.% carbonate electrolyte powder. The 54 wt.% sample has mostly submicron pores in the range 0.1–1 μm, while the 42 wt.% sample has a bimodal distribution

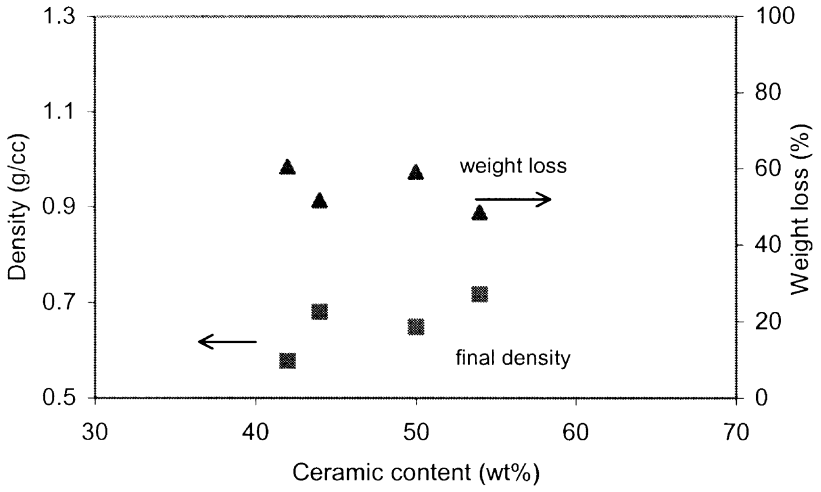

Fig. 5. Change in density and weight of matrix after heating to 650 °C.

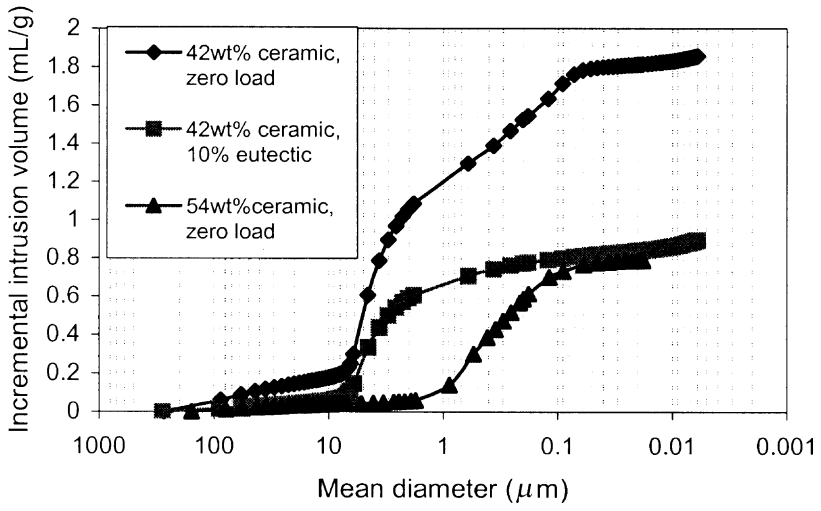

Fig. 6. Pore size distribution of matrix with and without carbonate electrolyte.

with pores in the sub-micron (0.07–0.6 μm) and micron (2–6 μm) range. The larger pores in 42 wt.% ceramic sample could have resulted from volatilisation of a larger quantity of organic additives. The sample with electrolyte has only the micron level pores indicating filling of the submicron pores by the electrolyte. This is expected since the driving force for intrusion of pores by the molten carbonate is capillary pressure.

The earlier results indicate that the ceramic content of the slurry influences the porosity as well as pore size distribution of the matrix; higher ceramic content leads to narrower pore size distribution and optimum porosity.

4. Summary

The components for MCFC have been fabricated with the required properties and the optimum processing conditions have been identified. The characteristics of the components are influenced by the processing conditions of the green tapes and the sintering conditions. The anode undergoes reduction in porosity in all the size ranges after cell testing. The cathode shows development of small pores as a result of lithiation and oxidation as well as reduction in porosity. The characteristics of the matrix are strongly influenced by the slurry composition. Tapes with higher ceramic content show narrow pore size distribution in the submicron range and the optimum porosity. Samples exposed to elevated temperatures in the presence of carbonate electrolyte did not develop any cracks or shape change.

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