

Short communication

Development of alpha lithium aluminate matrix for molten carbonate fuel cell

Vidya S. Batra^{a,*}, Shivani Maudgal^b, Sanjay Bali^a, Prahlad K. Tewari^a

^aTata Energy Research Institute, Darbari Seth Block, Habitat Place, Lodhi Road, New Delhi 110003, India

^bSchool of Environment Management, Guru Gobind Singh Indraprastha University, Delhi, India

Received 16 April 2002; accepted 12 June 2002

Abstract

The problems of stability associated with conventional gamma lithium aluminate matrix has prompted interest in development of alpha lithium aluminate matrix for molten carbonate fuel cells (MCFCs). Preparation of alpha lithium aluminate matrix using the technique of tape casting and the characteristics of the matrix are described. A matrix with a pore size in the range 0.9–0.2 μm and a porosity of 70 vol.% can be obtained. Cell testing with the alpha matrix gives satisfactory performance, with a maximum open-circuit voltage of 1000 mV.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Molten carbonate fuel cell; Alpha lithium aluminate matrix; Tape casting; Pore-size distribution

1. Introduction

The electrolyte matrix of a molten carbonate fuel cell (MCFC) is comprised of molten carbonate held within the fine pores of an inert support material to form a paste-like structure at the operating temperature of 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 gamma lithium aluminate. In recent studies, however, it has been observed [2,3] that gamma lithium aluminate not only undergoes particle growth, but also transforms to alpha lithium aluminate. The matrix from cells run for long duration showed extensive transformation of gamma to alpha [4]. In order to understand the transformation, out-of-cell tests have been conducted [5,6]. It was found that at 650 °C, gamma lithium aluminate containing traces of alpha lithium aluminate transformed to alpha. It was also found that alpha lithium aluminate and alpha + beta lithium aluminate remained stable. As a result of these studies, alpha lithium aluminate has become the preferred choice for the matrix support.

In this paper, alpha lithium matrix is fabricated by means of the technique of tape casting and the performance of MCFC monosell using this matrix is reported.

2. Experimental procedure

2.1. Matrix fabrication

The characteristics of the starting alpha lithium aluminate powder (from Cyprus Foote Mineral Company, USA) are shown in Table 1. The matrix was prepared by tape casting using a non-aqueous slurry, since the matrix was being used in green form in close contact with hygroscopic carbonate electrolyte. The binder and plasticizer were polyvinyl butyral and polyethylene glycol, respectively, and the solvent was a mixture of butanol and *iso*-propyl alcohol. The ratio of binder, plasticizer and lithium aluminate in the slurry was varied to obtain a ceramic loading in the range 47–59 wt.%. The slurry was prepared by ball-milling the ceramic powder for 1 h in the solvent which contained the binder and plasticizer. Subsequently, green tapes of 5 cm \times 5 cm dimension were prepared by tape casting on a smooth glass surface. To obtain green tapes for cell testing, select compositions were scaled up to a size of 15 cm \times 30 cm.

2.2. Characterization

To determine the change in characteristics due to heating and binder burn out, pieces of known weight and volume from the green tape were heated to 650 °C in air. The porosity and pore-size distribution of the matrix after binder

* Corresponding author. Tel.: +91-11-4682100/11x2618;

fax: +91-11-4682144/45.

E-mail address: vidyasb@teri.res.in (V.S. Batra).

Table 1
Characteristics of lithium aluminate powder

Lithium oxide	22.7%
Aluminum oxide	74%
Surface area	10 m ² /g
Particle size	99.5%, 325 mesh

burn out was determined using a mercury porosimeter (Poresizer 9320, Micromeritics, USA).

2.3. Cell assembly and testing

Testing was conducted in a 10 cm × 10 cm cell which had an electrochemical active area of 8 cm × 8 cm. The anode was comprised of tape cast and sintered nickel reinforced with aluminum, and had a typical porosity of 65 vol.% and a pore size in the range 3–6 μm. The cathode was comprised of tape cast and sintered nickel with a typical porosity of 80 vol.% and a pore size in the range 6–12 μm. For the matrix support material, two tapes of alpha lithium aluminate were used. The electrolyte was a eutectic mixture of lithium and potassium carbonates. The electrolyte loading was 194%, where 100% loading corresponds to the electrolyte volume required to fill all the pores of the matrix. The characteristics of the components are shown in Table 2. The components were housed in Stainless-Steel 310 end-plates which had channels for gas passage. The cell assembly was heated using external heaters and programmable temperature controllers, with CO₂ flowing through the electrochemically active area to prevent oxidation of the electrodes.

Table 2
Characteristics of cell components

Criteria	Anode	Cathode	Matrix (I)	Matrix (II)
Length (cm)	10	10	10.5	10.5
Breadth (cm)	10	10	10.5	10.5
Weight (g)	10.74	11.53	22.40	21.91

The assembly was heated at a slow rate with soak times at 150, 350 and 550 °C, before reaching the cell operating temperature of 650 °C.

The gas was supplied from gas cylinders and the flow rate was controlled by fine control rotameters (Instrument Engineers Pvt. Ltd., India). After the cell assembly reached the operating temperature, the CO₂ supply was stopped and hydrogen was passed at the anode. A mixture of CO₂ and O₂ was passed at the cathode for the oxidation reaction. The cell assembly was maintained at 650 °C to allow the open-circuit voltage to reach its highest stable value.

3. Results and discussions

The matrix green tapes were smooth, flexible and easy to remove from the substrate, irrespective of the ceramic loading in the slurry. The samples after heating to 650 °C in air did not show any change in area or cracking. With increasing ceramic content, the weight loss was reduced and final density was increased, as shown in Fig. 1. This is due to the presence of decreasing volatile content in the green tapes with increasing ceramic content.

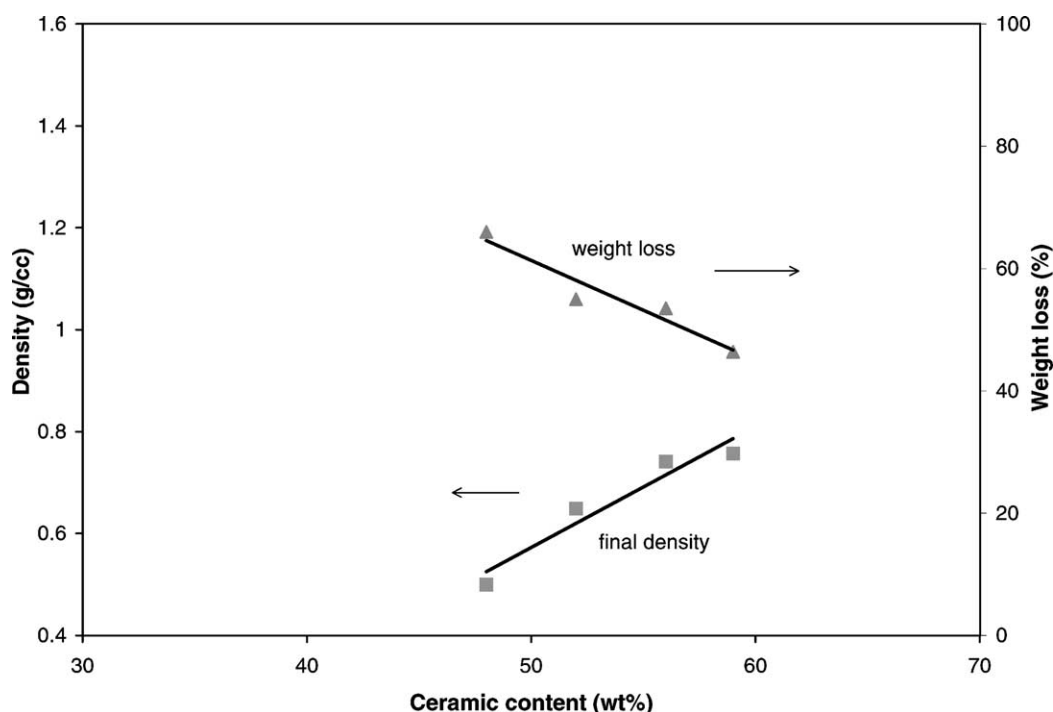


Fig. 1. Change in density and weight of matrix after heating to 650 °C.

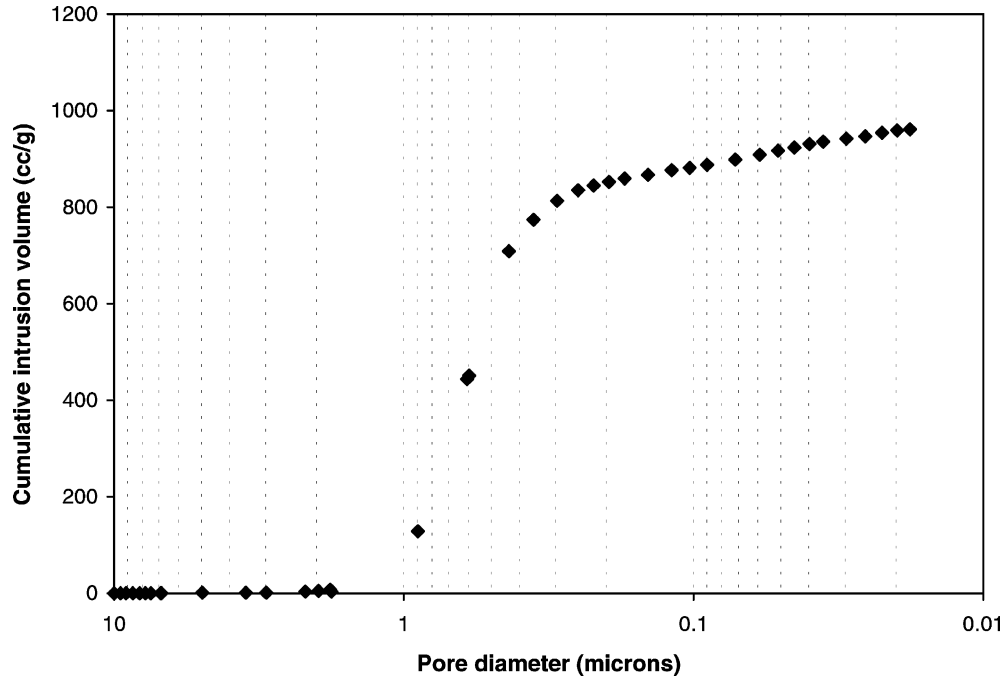


Fig. 2. Pore-size distribution of alpha lithium aluminate matrix.

Based on these observations, the slurry composition with 56 wt.% ceramic was chosen for scale-up to obtain tapes for cell testing. The larger tapes (15 cm × 30 cm) of this composition however developed cracks during drying. Therefore, scaling-up was attempted with a lower ceramic content

of 52 wt.%. This composition resulted in satisfactory large tapes. Porosity analysis of the sample after organic removal at 650 °C is shown in Fig. 2. The matrix has sub-micron pores in the range 0.2–0.9 μm and a porosity of 70 vol.%. This matrix was selected for cell testing.

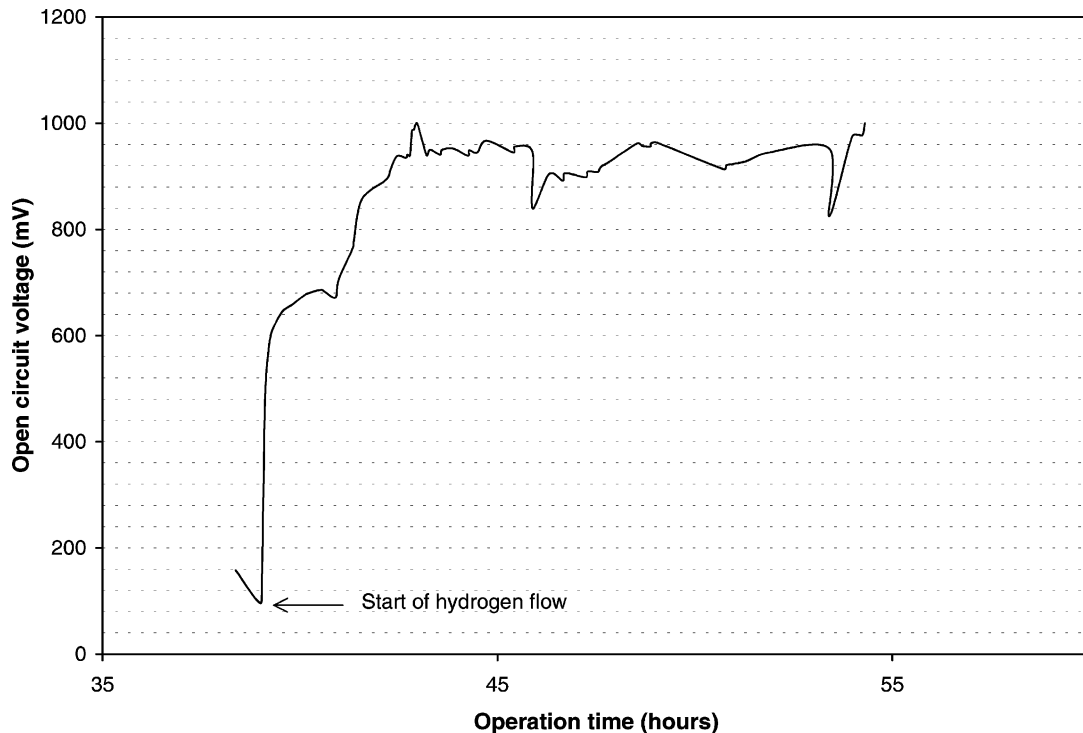


Fig. 3. Open-circuit voltage of monocell using alpha lithium aluminate matrix.

The results from the cell test are shown in Fig. 3. The cell reached the operating temperature after about 38 h and hydrogen flow was subsequently commenced. The cell voltage started to build-up and within 2 h rose to 672 mV. Subsequently, the cell reached 1000 mV and was stable between 850 and 1000 mV for the next 11 h. Due to hydrogen leakage in the cell assembly at this point, however, the cell had to be shut down. The maximum voltage was obtained with a hydrogen flow rate of 110 cm³/min, an oxygen flow rate of 50 cm³/min, and a cathodic carbon dioxide flow rate of 150 cm³/min. With increasing time, the flow rate of hydrogen and oxygen had to be increased to maintain the voltage. The hydrogen flow rate was increased up to a maximum of 250 cm³/min. The maximum flow rates of oxygen and carbon dioxide at the cathode were 70 and 240 cm³/min, respectively.

4. Conclusions

Alpha lithium aluminate tapes with suitable properties can be obtained by the tape casting technique using polyvinyl butyral as binder and polyethylene glycol as plasticizer. The matrix has sub-micron pores in the range 0.2–0.9 μm. Cell tests with the new matrix gave satisfactory performance with a maximum open-circuit voltage of

1000 mV and a stable value in the range 850–1000 mV for more than 10 h.

Acknowledgements

The authors acknowledge Dr. R.K. Pachauri, Director General, TERI, for providing the infrastructural facility to conduct the work. The technical assistance of Mr. Bhagwat Singh Bisht is acknowledged. This work was supported by the Ministry of Non-Conventional Energy Sources, Government of India and TERI.

References

- [1] J.R. Selman, L.J.M.J. Blomen, M.N. Mugerwa, Fuel Cell Systems, Plenum Press, New York, p. 345.
- [2] A. Sasaki, T. Shinoki, M. Matsumura, in: Proceedings of the Seminar on Fuel Cell, Orlando, Florida, 1996, p. 288 (abstracts).
- [3] M. Hori, T. Hayashi, Y. Shimizu, in: Proceedings of the Seminar on Fuel Cell, Orlando, Florida, 1996, p. 292 (abstracts).
- [4] K. Tanimoto, M. Yanagida, T. Kojima, Y. Tamiya, H. Matsumoto, Y. Miyazaki, J. Power Sources 72 (1998) 77.
- [5] K. Nakagawa, W. Ohzu, Y. Akasaka, N. Tomimatsu, Denki Kagaku 65 (1997) 231.
- [6] S. Terada, I. Nagashima, K. Higaki, Y. Ito, J. Power Sources 75 (1998) 223.