

## Molten Carbonate Fuel Cell Development Activities at CECRI, Karaikudi

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A research and development program on molten carbonate fuel cells (MCFC) has been started at Central Electrochemical Research Institute, Karaikudi since early 1992. After four years of basic studies and research, materials and their fabrication technologies were established. The project was then funded and supported by the Ministry of Non-conventional Energy Sources (MNES), New Delhi. During this period the parameters for making the electrodes and matrix materials by tape casting technique have been optimised. Focus was towards the design and fabrication of SS316 end plates. Better control of the cell startup procedures was arrived at. Data from the bench scale tests are reported in this paper. Nearly 35 numbers of single cells with active electrode size 45 and 100 cm<sup>2</sup> were tested. The maximum current obtained was 7.62 A (168 mA/cm<sup>2</sup>) per cell at a cell voltage of 0.62 V with 45 cm<sup>2</sup> area cells and 10.5 A (105 mA/cm<sup>2</sup>) at a cell voltage of 0.67 V, with 100 cm<sup>2</sup> size electrodes. The data from the bench scale tests indicate that a power density greater than 100 mW/cm<sup>2</sup> is possible. Performance and endurance tests were also carried out.

*Key words:* Molten carbonate fuel cells, tape casting, electrolyte matrix

### Introduction

In India, the research and development programme on MCFC was first started as a small project at CECRI in 1992. The need for attempting on the development of MCFC has been described earlier [1-3]. This programme is exclusively aiming at high level of technological research in which electrochemistry and materials technology play an important role. The results achieved and the progress made under the preliminary work were also published [4-7]. Following this, a national R&D planning on MCFC technology development was prepared and submitted to the Ministry of Non-conventional Energy Sources (MNES), New Delhi [8].

Based on the above, a program on the development of MCFC technology at CECRI was sponsored by MNES in 1996. The objective of the project was to establish indigenous fundamental technology for the demonstration of MCFC mono-cells with performance higher than 0.70 V at 150 mA/cm<sup>2</sup> during the period May 1996 - Mar 1999. This article describes in detail the achievements made under this program including the status of cell component technology and operational experience of laboratory single cells and the current R&D activities.

### Experimental

#### Manufacture of cell components

##### *Preparation of the matrix material ( $\gamma$ - LiAlO<sub>2</sub>)*

A new proprietary technique for the synthesis of gamma - LiAlO<sub>2</sub> powder, called combustion synthesis was developed using various fuels for use as the matrix material in MCFC [9,10]. The particle size distribution and surface area measurements were also carried out. A reactor set up has been designed and fabricated to produce the same in a semi continuous manner to the required quantities. Now it is possible to produce  $\gamma$ - LiAlO<sub>2</sub> powder with uniform particle size distribution (7.9 - 19.1  $\mu$ m) with varying surface area (10 - 50 m<sup>2</sup>/g).

##### *Preparation of electrolyte matrix structures\**

Usually a eutectic mixture of Li<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> (62:38 molar ratio) is employed as the electrolyte. A porous tile of  $\gamma$ - LiAlO<sub>2</sub> is used as the matrix to hold the electrolyte. The nominal composition of matrix to electrolyte powder varies in the ratio 40:60 to 45:55 wt%. Tape casting was employed as the method to prepare thin (0.5 - 1.0 mm) tapes of electrolyte, matrix and matrix + electrolyte structures separately [11,12]. The composition of the tape casting slip and the conditions employed during the casting process are covered by a patent application [13]. Improvement in

the production of matrices both by aqueous and nonaqueous tape casting methods was effected by incorporation of ceramic fibre [14]. The TGA/DTA data of the tapes were also obtained to determine the firing schedule to be adopted during the cell startup.

#### *Preparation of porous electrodes*

Ni powder (INCO 255) was used to prepare the electrodes. Several batches of electrodes (< 1.0 mm thick) were prepared by loose powder sintering [15]. Ni + 10 wt % Cr powder (75 – 90  $\mu\text{m}$ ) was used to prepare the anodes. The cathode employed was a nickel electrode, usually oxidised to NiO and lithiated insitu inside the cell. In the tape casting process, the metal powders are mixed with the binder and the solvent (water) to make slurry and the slurry is cast into the shape of a tape by a Doctor blade assembly [16,17]. The TGA/DTA experiments on the tapes were also carried out to determine the firing schedule to be adopted during the sintering stage. The characteristics of the porous electrodes like density, shrinkage factor after the casting process and after the sintering stage, total volume porosity and the pore size distribution were also determined. Different methods of making the cathode catalysts were also attempted and reported [18].

#### **The cell assembly component fabrication and cell startup**

The design for the end plates to incorporate the test electrodes of square size and the test bench employed was described in Ref. 19. Cells with two different sizes 6.7 x 6.7 (45  $\text{cm}^2$ ) and 12.5 x 12.5 (150  $\text{cm}^2$ ) of electrodes and matrices were tested. A Ni perforated sheet on the anode side and an SS perforated sheet on the cathode side were used as current collectors. The matrix and electrolyte tapes rest on the full area of the end plates and were held in position in between the anode and the cathode. An assembly for testing a small 3  $\text{cm}^2$  size single cell was also fabricated [20].

The cell start up procedure and the profile employed were described earlier [21]. Initially the cells were started with  $\text{N}_2$  and  $\text{CO}_2$  on both the chambers. The cells were heated at a slow heating rate of  $1^\circ\text{C}/\text{min}$  and maintained at different intermediate stages for different duration up to  $500^\circ\text{C}$ . The reactant gases preheated to above  $150^\circ\text{C}$  were fed into the inlet manifolds. When the cell attained  $500^\circ\text{C}$ , the reactant gases were switched over to the following nominal compositions and heated up to  $650^\circ\text{C}$  and maintained at the same temperature.

Anode gas:  $\text{H}_2$  (80 vol. %) +  $\text{CO}_2$  (20 vol. %) at flow rates of 80 – 200 ml/min (minimum) and 400 – 600 ml/min. (maximum).

Cathode gas:  $\text{O}_2$  (33 vol. %) +  $\text{CO}_2$  (67 vol. %) at flow rates 50 – 100 ml/min. (minimum) and 200 – 300 ml/min. ( maximum).

## **Results and discussion**

### **Physical characteristics of electrodes**

Tape casting is a versatile method of making fuel cell components [11,17]. The slurry viscosity controls the physical properties of the tapes as reported earlier. The fabrication of electrodes and matrices with increased area requires not only increased slurry composition but also larger tape casting time, thereby increasing the difficulty in obtaining tapes of uniform thickness. Efforts are currently undertaken towards the development of tape casting process for large area components. The photograph (Fig.1) shows the electrode tape. By this method both the electrode and matrix tapes with thickness less than 0.5 mm were produced in the size range 30 x 40  $\text{cm}^2$ .

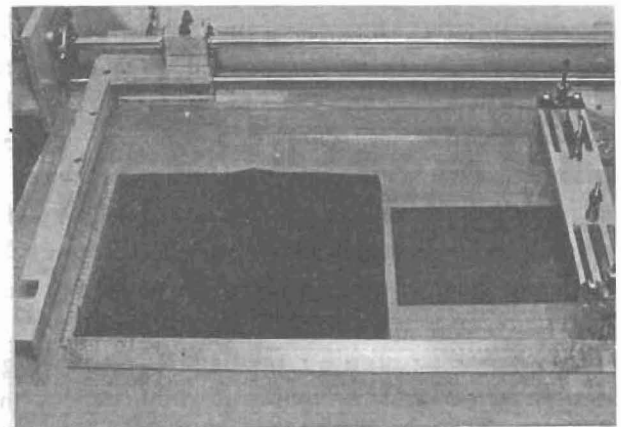


Fig. 1 photograph of the nickel tape 1000  $\text{cm}^2$

### **Performance of single cells with 3 $\text{cm}^2$ area components**

Both electrodes and matrix were cut into 3  $\text{cm}^2$  area circular shape and single cells were assembled and tested at different operating conditions. The voltage current characteristics obtained from a single cell with an electrode area of 3  $\text{cm}^2$  are shown in Fig. 2. The cells were discharged at various intervals of time at  $650^\circ\text{C}$  using the humidified fuel and dry oxygen at 50% utilisation. It is seen from Fig. 2, that the OCV is 1.09 V, which is closer to the theoretical value. The cell voltages were found to be 0.76 and 0.70 V at 150 and

200 mA/cm<sup>2</sup> respectively. The parameters like influence of gas flow rates and cell temperature etc. on the cell voltage and current density values is reported separately [22]. The physical characteristics of the electrodes like thickness, density and the cell voltage and current density values are reported in Table 1. The performance was found to be reproducible with other cells tested.

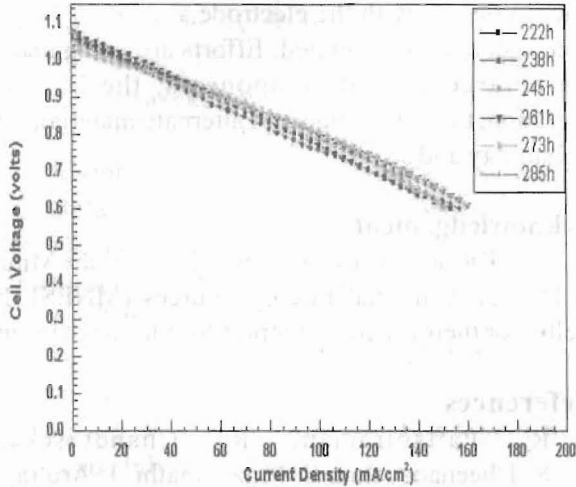


Fig.2. Discharge characteristics of MCFC at various intervals after 200 hours of operation at 650°C.

Table 1. Physical characteristics of cell components and cell performance

Sl. No.	Material	Thickness (mm)	Density (g/cm <sup>3</sup> )	Porosity (%)	OCV (V)	Current density (mA/cm <sup>2</sup> )
1.	Anode	1.42	2.800	60.89	1.059	150
	cathode	1.18	1.968	—		
	matrix	0.88	1.294	—		
2.	Anode	1.42	2.800	60.89	1.102	200
	cathode	1.18	1.968	—		
	matrix	0.89	1.294	—		
3.	anode	1.49	3.420	60.89	1.074	180
	cathode	1.04	1.970	—		
	matrix	0.89	1.700	—		

#### Performance data of the MCFC (mono-cells) with larger area

Based on the endurance test on smaller size cells nearly 35 cells have been tested. The best performance was noticed for cell no 22 with 45 cm<sup>2</sup> area cell components. This cell was discharged at a maximum current of 7.62 A (170 mA/cm<sup>2</sup>) at a cell voltage of 0.633 V and at a minimum current of 5.12 A (113 mA/cm<sup>2</sup>) at a cell voltage of 0.71 V. The cells exhibited an increase in the cell voltage during continuous discharge at constant current.

Figure 3 shows the cell assembly details of MCFC with 150 cm<sup>2</sup> components. Here also the same heating profile was employed for the cell startup except that the holding time at each temperature was higher in order to account for smooth and easy burning out of the binder materials. Cell No. 35 with electrodes (100 cm<sup>2</sup> active area) gave 10.5 A (105 mA/cm<sup>2</sup>) at a cell voltage of 0.67 V (The OCV was 1.032 V). The cell was discharged continuously for 500 hours at a constant load of 100 mA/cm<sup>2</sup>. The OCV and cell voltage characteristics are indicated in Fig. 4. No decay in cell voltage was noticed up to 550 hrs. The capacity obtained was 7.0 watts per cell. The above results indicate that the maximum power density realised in different cells range from 103 mW/cm<sup>2</sup> (for cell No. 14) and 109 mW/cm<sup>2</sup> (for cell No. 22). This value is very much close to the values (105 mW/cm<sup>2</sup> i.e. 0.70 V at 150 mA/cm<sup>2</sup> to 120 mW/cm<sup>2</sup> i.e. 0.75 V at 160 mA/cm<sup>2</sup>) reported by the various international developers of MCFC. The table also indicates the performance data of cells with 100 cm<sup>2</sup> area, where the maximum current density obtained was in the range 80-100 mA/cm<sup>2</sup>. Efforts are underway to improve the performance of these cells close to the value reported by others by proper design and optimisation of the parameters like gas distribution, gas flow rate and electrolyte content which may influence the cell performance.

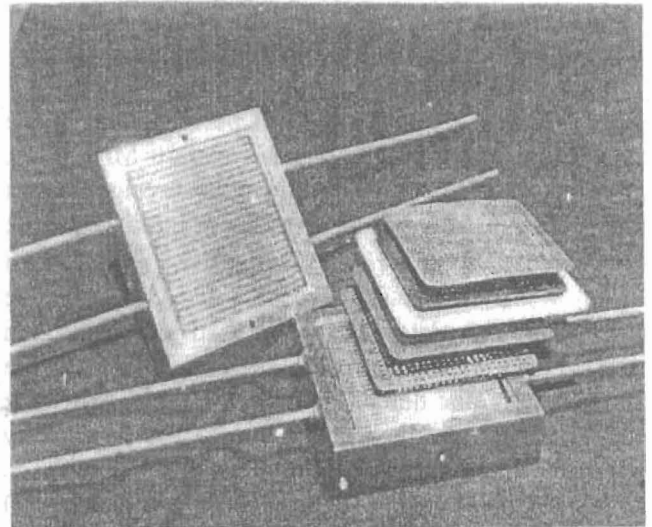


Fig.3. Cell components of MCFC (150 cm<sup>2</sup> area) electrodes, matrix, perforated current collectors and SS end plates.

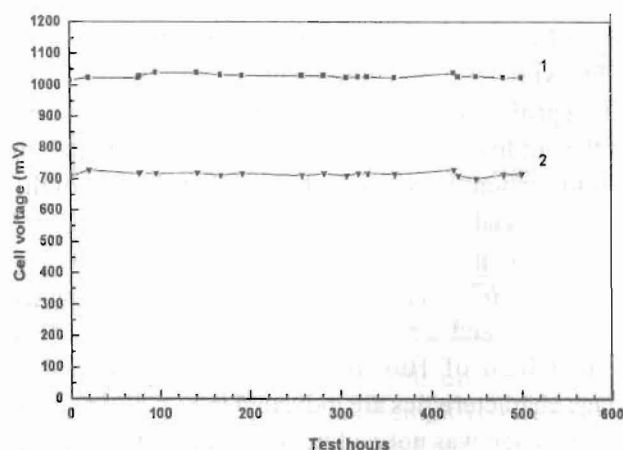


Fig.4. Continuous test data for cell No. 35: (1) cell voltage under open circuit conditions and (2) under discharge at 10.5 A (100 mA/cm<sup>2</sup>)

Table 2. Characteristics of MCFC cells tested

Sl. No.	Area (cm <sup>2</sup> )	Anode	Cathode	OCV (V)	Current (A)	C.d. (mA/cm <sup>2</sup> )	C. V. (V)	Hours of test
1.	45	Ni-Cr(CC)	TC(PO)	0.935	7.40	163	0.62	375
2.	45	Ni-Cr(TC)	Ni (TC)	0.970	2.77	62	0.63	530
3.	45	Ni-Cr(CC)	TC(EO)	0.953	7.62	170	0.63	700
4.	100	Ni-Cr	TC (IOL)	1.032	10.5	105	0.67	500

CC: Cold compaction and sintered

TC: Tape cast and sintered

IO: Insitu oxidised and lithiated

PO: Preoxidised

EO: Exsitu oxidised

### The current status

Based on the successful performance of the mono-cells a project proposal was submitted to MNES [23]. The Phase I of this project aims at the development of technology for assembly and testing of multi-cell stack of MCFC comprising 2 to 3 cells. During this period, all technical problems associated with the stack like edge sealing, bipolar plate design, gas distribution through internal manifolding etc will be attempted. Based on the above results, the demonstration of a multi-cell stack MCFC with 5-10 cells in the size range 100 W capacity will be attempted during 2002. This will be useful to assess our capability in scaling up the cell size to 450 cm<sup>2</sup> and building larger size MCFC stacks with output in the range 100–250 watts under phase II and in the range 500 W – 1.0 kW under phase III. The technology will be useful in scaling up the stack size to 10 kW and beyond which will find applications as standby power generation devices.

### Conclusion

Based on the development strategy described above, a steady progress has been made to develop indigenous MCFC technology. Following the establishment of the fundamental technology of manufacturing components and of operating 3 cm<sup>2</sup> single cells, the electrode area has been enlarged to 45 and 100 cm<sup>2</sup>. The single cell with the electrode area of 100 cm<sup>2</sup> has been successfully operated. Efforts are being made on the enlargement of components, the long term operation, the development of alternate materials, stack technology and so on.

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