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DEVELOPMENT OF MOLTEN CARBONATE FUEL CELLS (MCFC)

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Molten carbonate Fuel Cells (MCFC) are considered as the second generation fuel cell technology. They are characterized by high temperature of operation (923K) and high efficiency for energy conversion. Hydrogen derived from steam reformation of natural gas and coal can be used as a fuel. The heat generated from the cells can be utilized in the reformation reaction of the fuel.

The essential components of the MCFC are porous nickel electrodes, matrix for holding the molten electrolyte mixture, cell assembly hardwares, etc. Lithium aluminate ($\gamma - LiAlO_2$) is used as the matrix. $\gamma - LiAlO_2$ powder was prepared by high temperature solid state reaction of Li_2CO_3 with Al_2O_3 at 1273K. The γ - variety initially obtained at 873K was transformed into the γ -form at 1273K on prolonged heating. These powders were characterized by x-ray diffraction techniques.

Porous nickel electrodes were fabricated by loose powder sintering technique. Small prototype cells consisting of 10 and 20 cm^2 area electrodes were assembled. Lithium aluminate tiles were prepared by cold compaction and sintering and slurry casting techniques for the above. Current densities in the range 40 - 75 mA. cm^{-2} were obtained at a cell voltage of 0.7 V at 923K for short duration. A programme has been initiated to demonstrate higher capacity cells (10 watts per cell).

Key words: Molten carbonate fuel cell, γ - $LiAlO_2$ tile, porous nickel oxide, lithiated nickel oxide

INTRODUCTION

MCFC system offers striking advantages when compared with the other types of fuel cell systems [1]. The main advantages are its relatively high energy conversion efficiency (50%), low cost and the ability to adopt to the gaseous fuels derived from coal. As the operating temperature of the MCFC system is high, high power densities, without significant polarisation loss, become realisable. Noble metal electrocatalysts are not required to accelerate the electrochemical processes occurring in MCFC system. Further, MCFC system suits well to the cogeneration of electric power and high grade heat, thus offering an efficient utilization of the fuel energy. The schematic of a single cell of the MCFC is shown in Fig. 1. A single cell consists of a porous gas diffusion anode, an electrolyte retention matrix and a porous gas diffusion cathode. The molten electrolyte is suspended in the porous $\gamma - LiAlO_2$ matrix. The electrode reactions of MCFC are as follows;

Anode : $H_2 + CO_3^{2-} \longrightarrow H_2O + CO_2 + 2e^-$

Cathode : $CO_2 + \frac{1}{2} O_2 + 2e^- \longrightarrow CO_3^{2-}$

Overall : $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$

In this paper, the results obtained from the investigations carried out at CECRI, Karaikudi, on the preparation and characterization of the MCFC system components are presented. The performance characteristics of a few prototype MCFC systems assembled and tested are indicated. The problems and the prospects of the development of MCFC system with 10 watts per cell capacity are outlined.

EXPERIMENTAL

Electrolyte tile powder

Six batches of $LiAlO_2$ powder were prepared from the high temperature solid state reactions between γ -Al_2O_3 and Li_2CO_3 according to the following two steps sequence.

$$\gamma - Al_2O_3 + Li_2CO_3 \xrightarrow[873K]{10h} \gamma - LiAlO_2$$

$$\gamma - LiAlO_2 \xrightarrow[1273K]{24h} \gamma - LiAlO_2$$

The $\gamma - LiAlO_2$ powder thus obtained was subjected to x-ray diffraction (XRD) analysis, with Model 8030 x-ray powder diffractometer. The average particle size of the powder was 16 μm.

Electrolyte tiles

The heat of MCFC system is the tile made from $\gamma - LiAlO_2$ which holds the 62 mole% Li_2CO_3 and 38 mole% K_2CO_3 electrolyte at 923K operating temperature. It is therefore expected that fabrication of highly stable, thin and uniform tiles either alone or in combined form with the electrolyte salts is detrimental to the operation of MCFC system. Keeping this in view, to fabricate the $\gamma - LiAlO_2$ tiles with reasonably adequate functional requirements, two distinct schemes were formulated and put into practice. The experimental method adopted were: (i) cold compaction of $\gamma - LiAlO_2$ followed by sintering the compacts at 1273K for 3 h duration and (ii) hot compaction of $\gamma - LiAlO_2$ blended with the electrolyte in appropriate compositions (40 wt% of $LiAlO_2$ + 60 wt% of $K_2CO_3 + Li_2CO_3$ mixture) at 623K

Apart from these two schemes stated above, slurry casting of $\gamma - LiAlO_2$ powder with suitable compositions of binder and plasticizers into thin, smooth and uniform tapes was also standardized. These tapes were also sintered in air at 1473K for 2 h under a programmed heating rate of 60° per hour and a cooling rate of 100° per hour after removing the binder and plasticizer materials at 873K under a programmed heating rate of 30° per

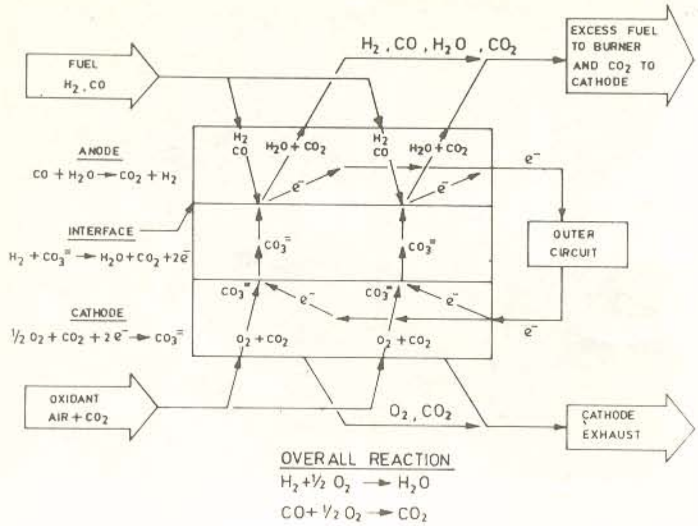


Fig 1: Schematic representation of a Molten Carbonate Fuel Cell

hour. The surface microstructures of the $\gamma - LiAlO_2$ tapes were analysed with scanning electron microscope (JEOL Model JSM 35-CF). Slurry casting of $\gamma - LiAlO_2$ powder mixed with carbonate mixture of the above composition was also tried and the green tapes were used directly in the cell assembly without prior sintering. The slow rise of the cell temperature to 923K resulted in the removal of the plastic materials. This procedure is called "in cell sintering" [2].

MCFC electrodes

The cathode was mostly composed of porous nickel oxide plate. The anode was porous nickel plate. In the fabrication of MCFC electrodes, several batches of porous nickel plates were prepared. The methods employed for the fabrication of electrodes involved slurry sintering or tape casting. The comprehensive representation of the details of the fabrication is presented in Table I.

TABLE-I: Characteristics of MCFC electrodes
Powder : carbonyl nickel type -255; Sintering : hydrogen atmosphere; 973K; Size : 4.4 cm diameter (15 cm^2 area)

Batch	Technique	Sintering time (h)	Thickness (mm)	Observation
1.	Slurry sintering	2	3.0	Nonuniform
2	Slurry sintering	3	3.2	Nonuniform
3.	Loose powder sintering	2	1.5	Smooth good
4.	Loose powder sintering	2	1.3	Uniform size and thickness
5.	Tape casting	1	0.8	Shrinkage during sintering

Lithiation of the MCFC cathodes was also carried out in order to provide electrocatalytic activity. In doing this, lithiated nickel oxide was prepared by solid state sintering method and the powder was characterised by XRD.

RESULTS AND DISCUSSION

The XRD pattern obtained with the $\gamma - LiAlO_2$ powder prepared by solid state sintering method is shown in Fig. 2. The data derived from this pattern is compared with the ASTM data and found to agree well with the phase composition of $\gamma - LiAlO_2$ [3, 4]. The data are presented in Table II.

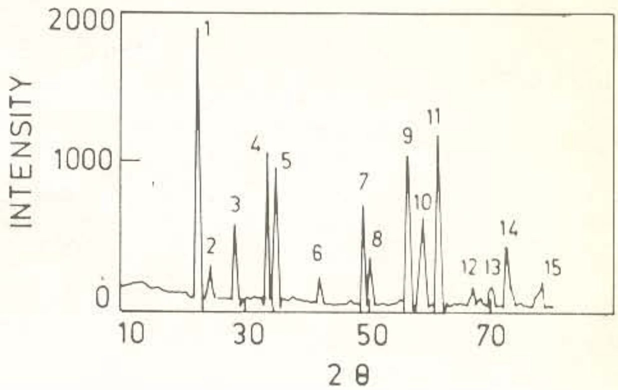


Fig 2: XRD pattern obtained with the $\gamma - LiAlO_2$ powder

The characteristics of the tiles fabricated from this $\gamma - LiAlO_2$ powder are presented in Table III. Different batches of $\gamma - LiAlO_2$ tapes were fabricated to obtain tapes with thickness in the range of 0.7 to 0.8 mm. The integrity of the tapes was fine with respect to their application in the MCFC environment. Optimization of the variables involved in this fabrication technique was carried out in order to reproduce the surface integrity of the $\gamma - LiAlO_2$ tapes.

TABLE-II: XRD data for lithium aluminate - A comparison between the sample prepared and the standard

	Observed				Standard			
	2θ (°)	d (A°)	I (Cps)	I/Io	2θ (°)	d (A°)	I/Io	hKl
1.	22.20	4.001	1930	100	22.296	3.984	100	101
2.	24.20	3.675	311	16	24.369	3.650	40	100
3.	28.20	3.162	604	31	28.267	3.155	50	111
4.	33.40	2.681	1111	58	33.395	2.681	90	102
5.	34.60	2.590	983	51	34.687	2.584	90	200
6.	41.60	2.169	233	12	41.599	2.169	30	211
7.	48.90	1.861	711	37	48.867	1.862	50	212
8.	50.00	1.823	395	20	50.228	1.815	30	113
9.	56.30	1.633	1066	55	56.252	1.634	30	310
10.	58.80	1.569	586	30	58.364	1.580	30	311
11.	61.30	1.511	1210	63	61.420	1.508	80	302
12.	66.90	1.397	185	10	66.943	1.397	10	321
13.	70.00	1.343	200	10	70.147	1.340	50	204
14.	72.40	1.304	438	23	72.428	1.304	70	322
15.	78.40	1.219	195	10	78.455	1.218	70	214

The agreement is 15/19

The SEM pictures of the $\gamma - LiAlO_2$ tapes prepared by the optimized method are shown in Fig. 3. The presintered tapes exhibit an uneven distribution of grains whereas it gets

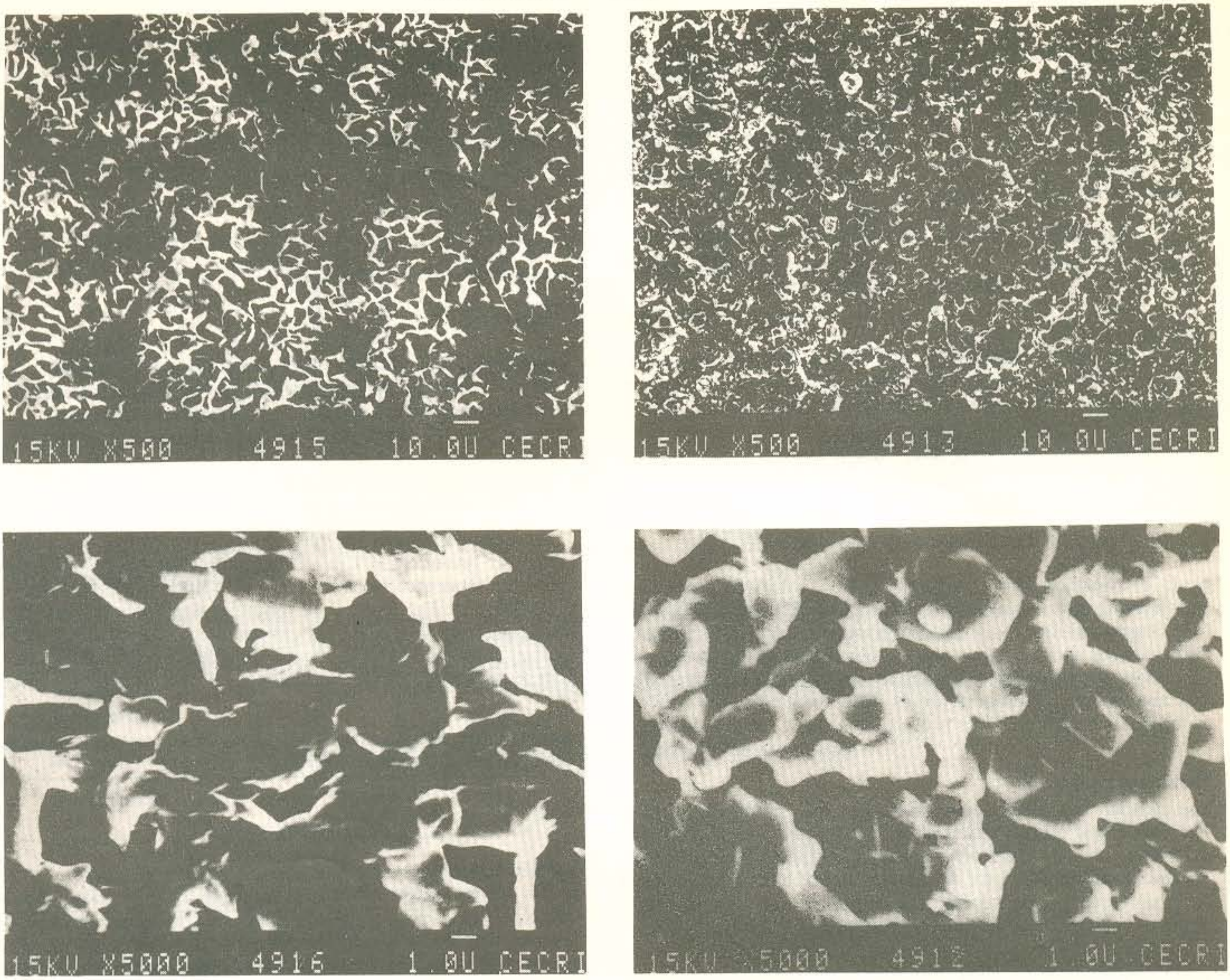


Fig 3: SEM pIctures of the $\gamma - LiAlO_2$ *tapes prepared by the optimised method (A) Presintered (B) Magnified version of 'A' (C) Sintered (D) Magnified version of 'C'*

integrated after subjecting the green tapes to standardised sintering procedures.

MCFC cathodes

The XRD pattern obtained with lithiated nickel oxide powder is shown in Fig. 4. The data derived from this pattern are compared with ASTM data to arrive at the phase composition [5]. The lithiation of porous nickel cathodes for the MCFC was done in two ways. The porous nickel plates prepared was dipped in a known quantity of aqueous solutions of Li_2CO_3 and subjected to heat treatment in order to enrich the pores with lithium. Alternatively, the nickel 255 powder was soaked in a known quantity of Li_2CO_3 aqueous solution for a given duration and then dried to fabricate porous plates by compaction followed by sintering. In both these methods, lithium could be loaded into the porous nickel electrodes resulting in the formation of lithiated nickel oxide while sintering in air. In all the cases, XRD pattern confirms the phase composition of $Li_2Ni_8O_{10}$.

MCFC assembly

By employing the porous nickel anodes, porous lithiated nickel oxide cathodes and porous $\gamma - LiAlO_2$ tapes loaded with 62 mole % Li_2CO_3 and 38 mole % K_2CO_3, MCFC units were assembled. In total, 23 unit cells were fabricated and put into test. The sizes of the electrodes and the electrolyte retention tapes were initially 3 cm^2 upto 10 unit cells. Figure 5 shows the single cell components and assembly. The sizes of the MCFC components were scaled upto 20 cm^2 active area so as to realise high discharge current densities. The characteristic performance data of the MCFC unit cells are presented in Table IV. Single cell performance of 0.88V at 80 $mA.cm^{-2}$ (1.5 watts per cell) has been realised. It has been observed that problems arising out of the cracks developed in the tapes with time is detrimental to the life of the cells.

CONCLUSION

The experimental results obtained in our efforts to fabricate the MCFC components with desired characteristics match well with the data available in the literature [6–11]. Based on the results reported in this paper, the authors envisage to demonstrate laboratory scale MCFC units with a capacity of 10 W per cell and to demonstrate 1 kW MCFC in three stages of development (10, 100 and 1000 watts) during the next three years. The programme

TABLE-III: Characteristics of the $\gamma - LiAlO_2$ tiles fabricated by tape casting technique

Batch	Weight (g)	Composition	Mixing	Thickness (mm)	Remarks
1.	30	Combined tape	Attritor milling	0.7–0.8	Blisters on the surface
2.	35	Combined tape	Attritor milling	0.7–0.8	Blisters on the surface
3.	70	$\gamma - LiAlO_2$ + starch	Ball milling	0.7–0.8	Good
4.	35	$\gamma - LiAlO_2$ + starch	Attritor milling	0.7–0.8	Good
5.	50	Combined tape	Attritor milling	0.7–0.8	Good
6.	50	Combined tape	Ball milling	0.7–0.8	Not good
7.	50	$\gamma - LiAlO_2$ + starch	Attritor	0.7–0.8	Not good

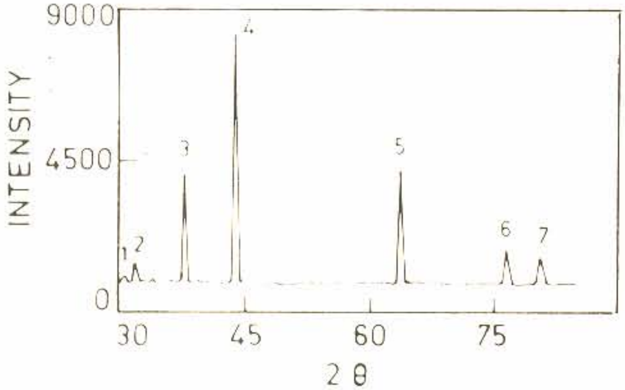
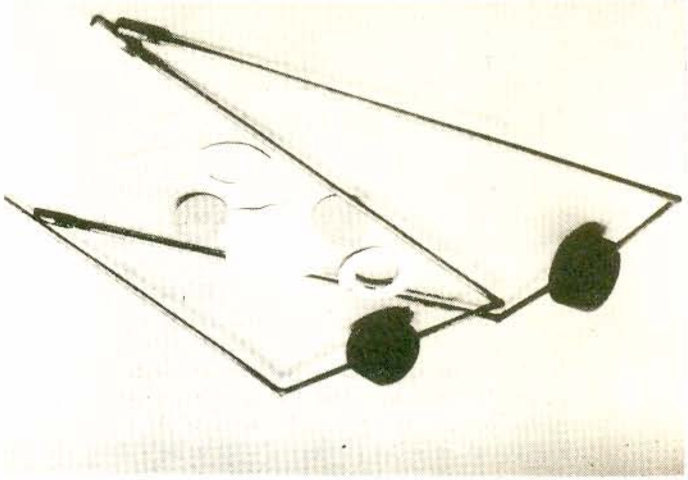
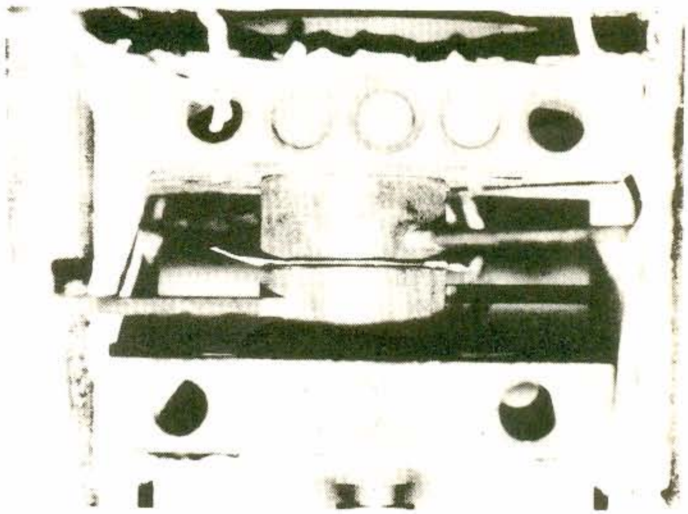


Fig 4: XRD pattern obtained with the lithiated nickel oxide powder



(A)



(B)

Fig 5: Photographs of the MCFC system (A) Components; (B) Cell assembly (10 cm² area electrodes)

of work includes multicell stack design and testing, kinetic studies including the influence of gas composition of the anode fuel and the pressure of CO_2 on the performance and the study of other problems namely, anode creep, cathode dissolution, electrolyte management, corrosion of stack materials, current collectors, wet seals and gas crossover management of the fuel on the performance of MCFC stacks.

TABLE-IV: Performance characteristics of MCFC single cells at 923 K

Cell No.	Electrode area (cm^2)	OCV (V)	Current drain (mA)	CV (V)	Time of testing (h)
2	3	0.820	30	0.60	3
7	3	0.863	40	0.62	5
17	10	0.850	300	0.60	15
21	10	0.855	850	0.65	10
23	20	1.040	1700	0.88	12

REFERENCES

1. R Pattabiraman, R Chandrasekaran, S Muzhumathi, I Arul Raj, S Dheenadayalan and V V Giridhar, *J Sci Ind Res*, **50** (1991) 661
2. J Nikura, K Hatoh, N Taniguchi, T Gamo and T Iwaki, *J Appl Electrochem*, **20** (1990) 606
3. JCPDS Powder Diffraction Data File - 18; Card number-714
4. M Marezio and J P Remeika, *Acta Crystallogr.* **19** (1965) 396
5. JCPDS Powder Diffraction Data File-23; Card number-362
6. K Hatoh, J Nikura, N Taniguchi, T Gamo and T Iwaki, *Denki Kagaku*, **57** (1989) 728
7. L Plomp, E F Sitters, C Vessies and F C Eckes, *J. Electrochem Soc*, **138** (1991) 629
8. J M Fisher, P S Bennett, J F Pignon, R C Makkus, R Weewer and K Hemmes, *ibid* **137** (1990) 1493
9. S Freni, N Giordano and S Cavallaro, *J Appl Electrochem*, **20** (1990) 804
10. Sei Takashima and Keizou ohtsuka, *Hitachi Rev*, **37** (1988) 171
11. P Van Dijkum and K Joon, *J Power Sources*, **29** (1990) 77