Design and Operation of a Standard 3 cm² Size Molten Carbonate Fuel Cell (MCFC) at 923 K

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A single molten carbonate fuel cell (MCFC) with an effective area of 3 cm² was designed and operated at 923 K. The cell was operated for 500 h using a standard gas compositions. Pre-sintered Ni-Cr (10 wt.%), insitu lithiated nickel oxide and an un-sintered tape of lithium aluminate were used as anode, cathode and electrolyte retention matrix respectively. The gas chamber and electrode holders were made up of SS 316. Perforated Ni and SS were used as the current collectors for the anode and cathode respectively. The electrolyte employed was a eutectic mixture of lithium and potassium carbonate (62:38 mol.%), which is normally in a molten state at the cell operating temperature of $H_2 + CO_2$ (80:20) as fuel and $O_2 + CO_2$ (67:33) as an oxidant. The performances of the single cell at various temperatures with different gas compositions were studied. Various parameters influencing the performance of the single cell MCFC are discussed.

Key words: Molten carbonate fuel cells, $LiAlO_2$ matrix tape, single cell assembly

Introduction

The molten carbonate fuel cell (MCFC) represents an efficient device for the conversion of chemical energy into electrical energy [1,2]. One of the main attractive features of the fuel cell system is its high fuel to electricity efficiency (45-65 %) based on the lower heating value of the fuel. A typical fuel cell assembly consists of a porous nickel anode and porous lithium doped nickel oxide cathode. They are separated by an electrolyte structure (62 mol.% Li_2CO_3 and 38 mol.% K_2CO_3) contained within a porous ceramic lithium aluminate matrix. The cell is operated at 923 K.

Efficient fuel cell operation requires that the electrodes must contain sufficient electrolyte to maintain the electrode/electrolyte/reactant gas necessary for the electrochemical reaction. Ideally, the electrodes with high surface area and porosity of 70 – 80 % with mean pore diameter in the range 10 – 15 µm were reported to be suitable. The life expectancy of the electrode structures is also aimed towards 40000 h for successful commercialisation of MCFC [3].

The MCFC will have an OCV of 1.075 V. The current from the cell will depend upon the area of the electrode. A typical laboratory cell will have a voltage of about 0.7 V with a capacity ranging from 0.10 – 0.15 watts per cm². A preliminary investigation on the fabrication of electrode and matrix materials was undertaken and the performance in 3 cm² size single cells is reported in this paper.

Experimental
Preparation of porous electrodes

The tape casting process was used to prepare larger area electrodes [4, 5]. The process involves preparation of slurry of nickel powder with suitable binder and plasticizer and casting it on a glass substrate using a doctor blade assembly. The cast bodies were removed from it after 12 h of curing and stored. The green nickel tapes were characterized for the thickness, shrinkage factor, and density values. The electrodes were reinforced using an SS wire mesh, which provided the mechanical strength during handling and also served as a current collector.

Characterisation of green tapes and porous electrodes

A PL thermal systems model STA 1500, Differential Thermal Analyser was employed to study the TGA and DTA characteristics of the green tape electrodes. A heating rate of 10 K/min was employed in air. The results were used to determine the thermal

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heat treatment schedule to be followed for the sintering procedure. They were sintered in hydrogen atmosphere at temperature 1073 K in a programmable furnace controlled at 1 K/min. heating rate. The sintered samples were also characterized for sintered density, shrinkage after sintering.

Preparation of electrolyte matrix structures

A porous tile of γ - $LiAlO_2$ is used as the matrix to hold the electrolyte and the electrolyte layer was the eutectic Li_2CO_3-K_2CO_3 mixture. The nominal composition of matrix to electrolyte powder varies in the ratio 40:60 to 45:55 wt%. The electrolyte and the matrix layers were prepared as thin (0.5 – 1.0 mm) tapes by tape casting technique as reported [6].

Single cell assembly

The single cell set up is similar to the one described in literature [7] and is shown in Fig.1. It employs three sets of concentric alumina tubes of desired lengths. Both the electrodes are of circular shape of 3 cm² area. The anode rests on a perforated Ni current collector placed over an SS cup, which rests on the inner alumina tube. The SS cup was welded to an SS pipe for hydrogen inlet from the bottom and also to an SS wire for current collection. The cup portion was given a sand blasting treatment and plated with Ni. This tube was carefully inserted into another alumina tube. Both the tubes rest on two SS plates, which were held in a cell holding system with screws. The two tubes were positioned in such a manner, that the outer tube looks like a collar for the electrode and their top surface is flat. Then the matrix (with same dia as that of the second tube) of 4.2 cm² area was placed over it. An identical alumina tube was placed from the top and held in position by the top SS plate. Weighed quantity of electrolyte powder with exact loading (100–300 mg/cm²) was poured into it. Or an electrolyte tape followed by a matrix tape can also be used. The cathode and current collector were placed over it. Again the cathode gas holder and the inner alumina tubes were inserted in an inverted fashion and held in position by the top SS plate of the holder with spring loaded screws. The cell assembly at the central portion was covered with another alumina tube and surrounded by a furnace assembly. The cathode gas inlet was from the top. Provisions were also made for electrolyte addition, temperature measurement and to keep a reference electrode in the matrix. The complete assembly is shown in Fig. 2.
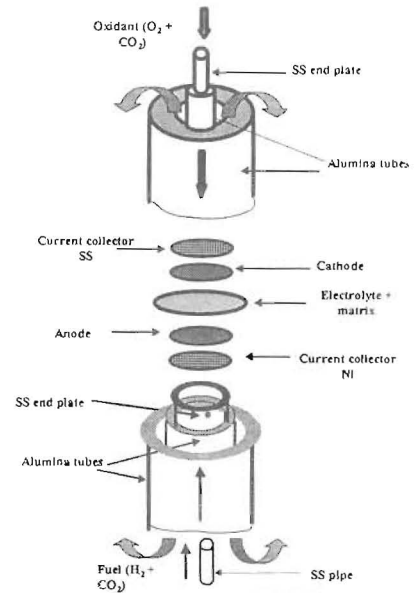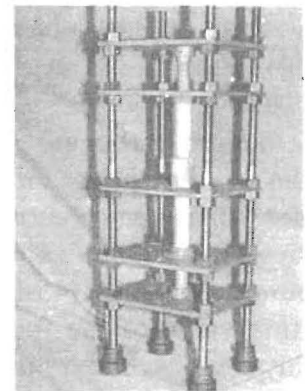

Fig. 1. MCFC cell components

Fig.2. Photograph of the single cell (MCFC) assembly (3cm²)

In cell tests

The cathode employed was a nickel electrode, usually oxidised to NiO and lithiated insitu inside the cell. Cell tests were carried out using the above as the cathodes and a Ni-Cr sintered anode in the MCFC test setup at 923 K. The anode thickness was 0.65 mm and the overall porosity was 55-60% with a mean pore dia of 7.0 μm.

The cell startup procedure was described elsewhere [8]. Initially the cells were started with N_2 and CO_2 on both the chambers. The cells were heated at a slow heating rate of 1 K/min and maintained at different intermediate stages for different duration up to 673 K. In the temperature range 673-773 K, H_2 and CO_2 gases (10:90 v/v) were passed on both the chambers. When the cell attained 773 K, the reactant

gases were switched over to the following nominal compositions and the cell was further heated up to 923 K and maintained at the same temperature. The reactant gases humidified at 333 K and preheated to above 423 K were fed into the inlet manifolds.

Anode gas: H_2 (80 vol.%) + CO_2 (20 vol.%) at flow rates of 100 ml/min (minimum) and 400 ml/min. (maximum).

Cathode gas: O_2 (33 vol. %) + CO_2 (67 vol. %) at flow rates 100 ml/min. (minimum) and 200 ml/min. (maximum).

The discharge experiments were carried out at different anode and cathode gas flow rates and the measurements were also made at 873 and 923 K.

Results and discussion

Physical characteristics of the green and sintered electrodes

Tape casting method has been described as a versatile method of making smooth, flat and thin substrates with larger geometrical area and found to be a suitable method for preparing fuel cell components [9]. The parameters influencing the tape casting of nickel powder by an aqueous slurry process using polyvinyl alcohol as binder have also been investigated. Tape casting with aqueous slurries has several advantages over non-aqueous method in that the former involves handling of nontoxic materials and vapors[10]. The first part of the work was to obtain a crack free green tape. This depends upon the good choice of the constituents of the slurry and on their quantitative optimisation.

The binder burnt-out conditions were also evaluated by TGA study. The TGA and DTA analysis of the green nickel tapes determine the sintering conditions. From the DTA/TGA results it was inferred that initially, there is a steady weight loss up to 383 K indicating that water from the green tape is removed. On further heating, a secondary weight loss is noticed up to 643 K indicating the plasticizer and binder materials is removed. Nickel oxidation starts at temperature above 673 K in air. This was used in determining the temperature profile during the sintering stage (Fig. 3).
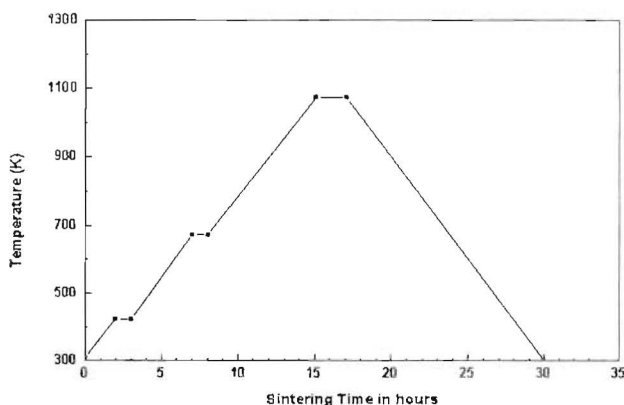

Fig. 3. Sintering profile of green Ni tape.

Consequently the electrodes were sintered in H_2 atmosphere at a slow heating rate of 1 K/min, with intermittent soaking stages at 423 K for 3 h and 673 K for 3 h to remove the inorganic and organic constituents. The final sintering temperature was at 1073 K (173 K for Ni-Cr) for one hour and cooled to room temperature at 1 K/min.

Table 1 indicates the characteristics of green tapes and the sintered electrodes prepared from these tapes after controlled sintering. Both shrinkage factors, density values of the green and sintered plaques and the final porosity values are reported. The density of the green compact depends upon the binder content (wt.%), slurry composition, solvent (water) content, plasticizer amount and casting rate [11].

Cell startup procedure

Changing over to the gas composition to hydrogen + CO_2 mixture at 673 K will retard oxidation of the anode. At 773 K the molten carbonate electrolyte melts and penetrates into the matrix. A part will also diffuse into the anode and cathode. The extent of filling on the electrodes depends upon the porosity and pore size distribution of the electrodes. This is estimated to be around 30 vol. % by observing the increase in the weight of the electrodes. The matrix placed at the top of the electrolyte powder fuses with the bottom matrix making as a single layer of electrolyte + matrix. At this stage the screws at the top SS plate were tightened so as to bring the electrode electrolyte in close contact.

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This avoids the cell thickness and gas leak also. Change of cathode gas composition above 773 K to a gas composition rich in O_2 will result in lithiation and in cell oxidation of the cathode. The electrolyte loading upto 300 mg/cm² was found to be sufficient.

Table 1. Characteristics of MCFC components employed

Property	Anode	Cathode	Tile
Area (cm²)	3	3	7
Green tape thickness (mm)	1.10	1.25	0.83
Green Density (g/cc)	1.95	1.968	1.294
Sintered thickness (mm)	0.86	0.96	---
Shrinkage (%)	23.20	21.80	---
Sintered density (g/cc)	2.80	2.28	---
Sintering temp. (K)	1123-1173	923-973	---
Porosity (%)	61.0	72.50	---

Cell performance

Both the OCV and cell voltage at cell voltages at different temperature, discharge current densities for different gas flow rates were measured. Fig.4. shows the effect of anode gas flow rate on the cell performance at 873 K. The results from other experiments are also summarized in Table 2. There is a significant dependence of the OCV on the gas flow rates at 873 K. The observed OCVs initially increased and were almost the same at higher gas flow rates. At a constant value of cathodic gas flow rate, the change in flow rate values of anode gas resulted in a lower polarization initially, thereafter, the polarization was found to be higher. From the current density values it can be inferred that an optimum value of anode gas flow rate is 120+30 ml of $H_2 + CO_2$. The fuel

utilization is maximum. In a similar manner from the polarization curves obtained with the change of cathode gas at constant anode gas flow rate, the OCV steadily decreased, but the current density trend was in a similar fashion reaching a maximum at an optimum flow rate value. Any amount of increase in flow rates thereafter will not be helpful.

Table 2. Performance of a single cell MCFC at different gas flow rates at 873 K
Anode gas: $H_2 + CO_2$ and Cathode gas: $O_2 + CO_2$

Anode gas flow rate (ml/min)	Cathode gas flow rate (ml/min)	OCV (V)	Cell voltage (V)	Current density (mA/cm²)
80 + 20	33 + 66	1.017	0.607	146
120 + 30	"	1.036	0.601	150
160 + 40	"	1.054	0.600	110
200 + 50	"	1.056	0.609	116
80 + 20	33 + 66	1.063	0.603	120
"	50 + 100	1.056	0.604	110
"	75 + 150	1.045	0.621	103
"	100 + 200	1.040	0.609	100

The influence of OCV in the temperature range 873 –923 k was very small and did not follow any order for different gas flow rates. Table 3 compares the OCV, CV, discharge c.d. values at the nominal and optimum gas flow rates both at 873 and 923 K. At the normal flow rate, the OCV decreased with the temperature. But the discharge c. d. value was higher. At the optimum gas flow rate the OCV was higher at 923 K. It is noticed that the polarization curves resulted in higher discharge current densities at 923 K than that at 873 K. This can be attributed to the higher conductivity of the electrolyte at 923 K [12].

The endurance test was carried out at with optimum gas flow rates and shown in Fig. 5. The cell was tested for a period exceeding 500 h without any deterioration in its performance.
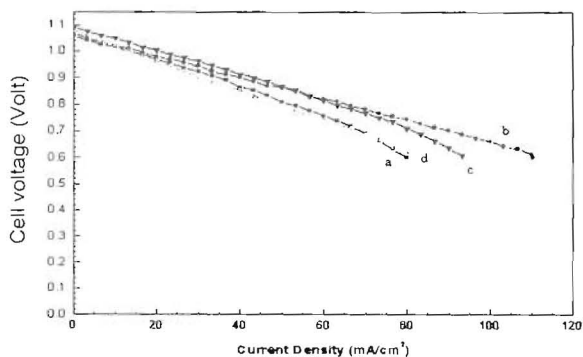
Fig. 4. Effect of anode gas flow rates on cell performance at 873 K.

(a) $H_2 + CO_2 = (80+20)$ ml/min., (b) $H_2 + CO_2 = (120+30)$ ml./min. (c) $H_2 + CO_2 = (160+40)$ ml./min.(d) $H_2 + CO_2 = (200+50)$ ml./min.

Table 3. Effect of temperature on MCFC single cell performance

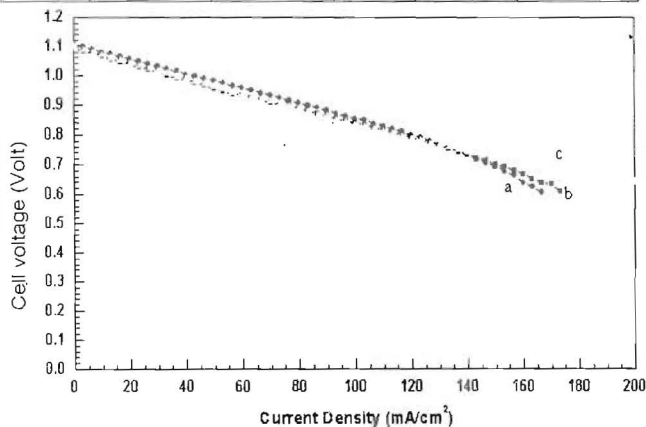| Temp. (K)	Anode gas flow rate (ml/min)	Cathode gas flow rate (ml/min)	OCV (V)	Cell voltage (V)	Current density (mA/cm²)
873	80 + 20	33 + 66	1.064	0.600	80
873	120 + 30	50 + 100	1.081	0.603	100
923	80 + 20	33 + 66	1.017	0.607	145
923	120 + 30	50 + 100	1.094	0.608	175

Fig. 5. Discharge comparison after 190, 200 & 215 Hours of operation at 650°C

(a) 200 h, (b) 300 h, (c) 500 h, at $H_2 + CO_2$: 200+40 ml/min. and $O_2 + CO_2$: 100+200 ml/min.

Conclusion

The experimental setup designed was successfully used for assembling a MCFC with a laboratory size components (3 cm²) for performance evaluation of the various components fabricated and for determining the influence of operating variables like gas flow rates, temperature on the cell performance.

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