

Preparation and characterization of cathode catalysts for molten carbonate fuel cells

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Three different methods were adopted to prepare the lithiated nickel oxide cathodes for Molten Carbonate Fuel Cell (MCFC). In the first method Ni electrodes with desired porosity were prepared and oxidized and lithiated inside the cell (in-situ method). Loose powder sintering, slurry casting and tape casting methods were followed to prepare the electrodes. In the second method, out of cell oxidation and lithiation of nickel powder was carried out by mixing nickel powder with lithium carbonate followed by oxidation in air at 650°C (ex-situ method) and then formed into the electrodes. In the third method, the pre-lithiated nickel catalyst was formed into an electrode by tape casting technique and the electrodes were subjected to in cell or out of cell oxidation and sintering. The physico-chemical characterization of the catalyst and the electrodes were obtained by XRD and mercury porosimetry respectively. The performance of the electrodes was evaluated in single cell MCFC with 45 cm² area electrodes at 650°C.

The molten carbonate fuel cell (MCFC) represents an efficient device for the conversion of chemical energy into electrical energy^{1,2}. 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% Li₂CO₃ and 38 mol% K₂CO₃) contained within a porous ceramic lithium aluminate matrix. The cell is operated at 650°C.

Efficient fuel cell operation requires that the electrodes must contain sufficient electrolyte to maintain the electrode/electrolyte/reactant gas necessary for the electrochemical reaction. This requires careful control of the overall porosity and pore size distribution³⁻⁷. 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 cathode structures is also aimed towards 40000 h for successful commercialisation of MCFC⁸.

The following cathode properties were recognised as fundamental importance with respect to the cell performance⁹.

- High electronic conductivity at 650°C ($\sigma > 1 \text{ S.cm}^{-1}$).
- Low chemical reactivity and solubility in the electrolyte.
- Thermodynamic stability at 650°C in CO₃ electrolyte at different partial pressures of O₂/CO₂ mixtures.

- High electrocatalytic activity for the reduction reaction.
- Suitability for the fabrication of porous electrodes.

Various materials have been evaluated for cathodes for MCFC¹⁰⁻¹². Nickel oxide has been as the preferred cathode material¹³. A number of methods have been reported to prepare lithiated nickel oxide cathodes¹⁴⁻¹⁶. The most widely adopted is the in-cell lithiation technique, where a sintered nickel oxide plaque is used as the cathode. At the operating temperature of the fuel cell i.e., at 650°C, the nickel oxide is oxidised to NiO under in-cell conditions and Li₂CO₃ from the electrolyte reacts with the NiO making it lithiated. The oxidation and lithiation of NiO is reported to affect the electrical properties of the cathode in presence of the molten carbonate electrolyte¹⁷. Efficient porous cathodes were synthesized by incorporating a nickel polymer composite structure, which was subsequently oxidized in-situ.

In this paper the methods of pre lithiation of nickel cathode catalysts and then forming the electrodes have been reported. Both in cell and out of cell oxidation of lithiated electrodes were tried. The characteristics of lithiated nickel oxide electrodes prepared by different techniques are presented.

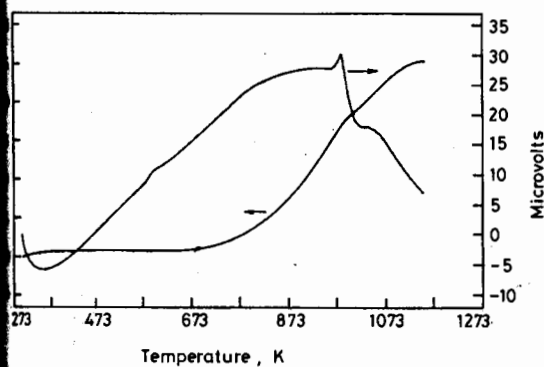
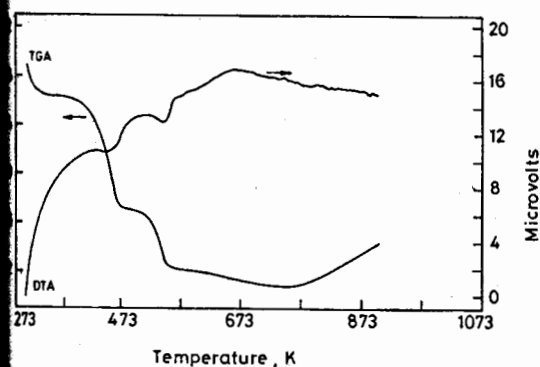
Fig. 1—TGA/DTA curve of Ni+Li₂CO₃ system

Fig. 2—TGA/DTA curve of an aqueous Ni tape

Experimental Procedure

Preparation of electrodes and conversion to lithiated nickel oxide by *in-situ* and *ex-situ* methods

Nickel powder (INCO 255) was used to prepare the electrodes. The metal powder was treated in hydrogen atmosphere as reported elsewhere²⁰. The resulting powder was sieved and powders below 200 mesh were used to prepare the electrodes. Several batches of electrodes were prepared by different techniques such as loose powder sintering (LPS), slurry casting (SC), tape casting (TC) etc. These electrodes were sintered in hydrogen atmosphere at 1073 K. The lithiated nickel electrodes were usually got lithiated inside the cell (*in-situ* method).

Preparation of lithiated nickel oxide catalyst

In the second method, the pre-lithiated nickel oxide catalyst was prepared by milling nickel powder and lithium carbonate in an organic medium (*n*-hexane). After drying at 100°C for 3 h, the solid-state reaction was carried out by heating the sample at 650°C in air for 24 h. Five different compositions of lithiated nickel oxide samples were prepared by this method. This

Table 1—Characteristics of lithiated nickel oxide samples

Sl. No.	Li (atom%)	Ni (atom%)	Surface area (m ² /g)	Av. Particle size (μm)	Lattice constant (Å)
1.	1	99	5.12	3.5	4.1760
2.	2	98	4.93	3.5	4.1712
3.	5	95	4.91	3.9	4.1659
4.	7.5	92.5	4.62	4.25	4.1614
5.	10	90	4.30	4.75	4.1579
6.	12	88	4.11	5.0	4.1535
7.	15	85	3.81	5.5	4.1482
8.	18	92	3.69	6.2	4.1428

powder was ground well in an agate mortar and sieved through ASTM 325 mesh. In a modified process of the above, the pre-lithiated nickel powder was prepared as above. After drying at 100°C, electrodes were prepared by tape casting technique. The electrodes were subjected to both oxidation and sintering at 650°C inside the cell and at 800°C outside the cell.

Physical characterization

The particle size distribution analysis of the powder was done with Malvern Particle Size Analyser Model 3600 U.K. The X-ray powder diffraction analysis was carried out in JEOL Model JDX 8030 X-ray Powder Diffractometer. A computer program based on the cubic lattice structure of NiO was used to obtain the lattice constant values. The surface area of the powder was determined by B.E.T. method using Surface Area Analyser (QUANTASORB, QS-14).

Preparation of porous electrodes

The tape casting process as reported earlier²¹ was used to prepare larger area electrodes. 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.

Table 2—Characteristics of nickel electrodes prepared by loose powder sintering and tape casting followed by sintering methods used as in-situ cathodes

Sl. No.	Green Thickness (mm)	Sintered Thickness (mm)	Shrinkage (%)	Green Density (g/cc)	Sintered Density (g/cc)	Porosity (%)
<i>Loose powder sintered Ni electrodes:</i>						
1.	UT	0.91	—	—	1.66	64.11
2.	UT	0.78	—	—	1.46	79.23
3.	T	0.66	—	—	2.87	62.34
4.	T	0.76	—	—	1.85	68.18
<i>Tape cast and sintered Ni electrodes:</i>						
5.	0.98	0.84	14.83	2.30	2.56	59.03
6.	0.95	0.75	21.17	1.99	3.19	59.06
7.	0.89	0.86	3.36	2.16	2.46	62.79
8.	1.22	0.87	28.44	1.53	2.31	72.91
<i>Pre lithiated, tape cast and out of cell sintered Ni electrodes</i>						
9.	1.12	0.90	19.20	1.52	2.22	71.91
10.	0.97	—	—	2.64	—	—
11.	0.69	0.67	—	1.74	1.98	68.41
12.	0.88	0.74	16.28	2.53	3.38	64.84
<i>Pre lithiated, tape cast and in cell sintered Ni electrodes</i>						
13.	0.89	—	—	1.74	—	—
14.	0.81	—	—	2.78	—	—
15.	1.25	—	—	2.89	—	—

*UT: hydrogen treatment not given and T: after hydrogen treatment if Ni powder.

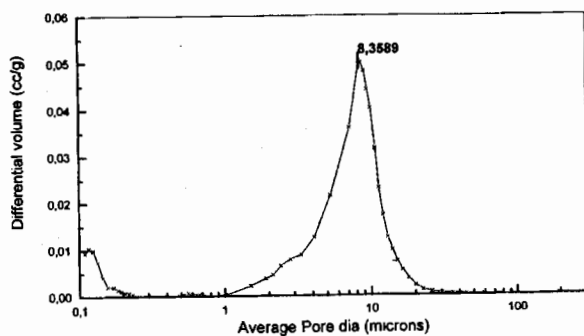


Fig. 3—Pore size distribution curve of a cathode

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°C/min was employed in air. The results were used to determine the thermal heat treatment schedule to be followed for the sintering procedure. They were sintered in hydrogen atmosphere at temperature 800°C in a programmable furnace controlled at a heating rate 1°C/min.

The sintered samples were also characterized by sintered density, shrinkage after sintering. The porosity values were determined by liquid absorption technique and the pore size distribution measurements were carried out using Micromeritics Model 9300 Pore Sizer. The micrographs of the porous electrodes were obtained using the Scanning Electron Microscope JEOL JSM 35CF at an accelerating voltage of 15 kV.

In cell tests

Cell tests were carried out using the above as cathodes and a Ni-Cr sintered anode in a MCFC setup as described earlier²² at 650°C. The anode thickness was 0.65 mm and the overall porosity was 55-60% with a mean pore dia of 7.0 μm. The electrolyte matrix was made up of γ-LiAlO₂ and the electrolyte layer was the eutectic Li₂CO₃-K₂CO₃ mixture. The electrolyte and the matrix layers were prepared by tape casting technique as reported elsewhere²³. The cell startup procedure was discussed earlier²².

Fig. 4—

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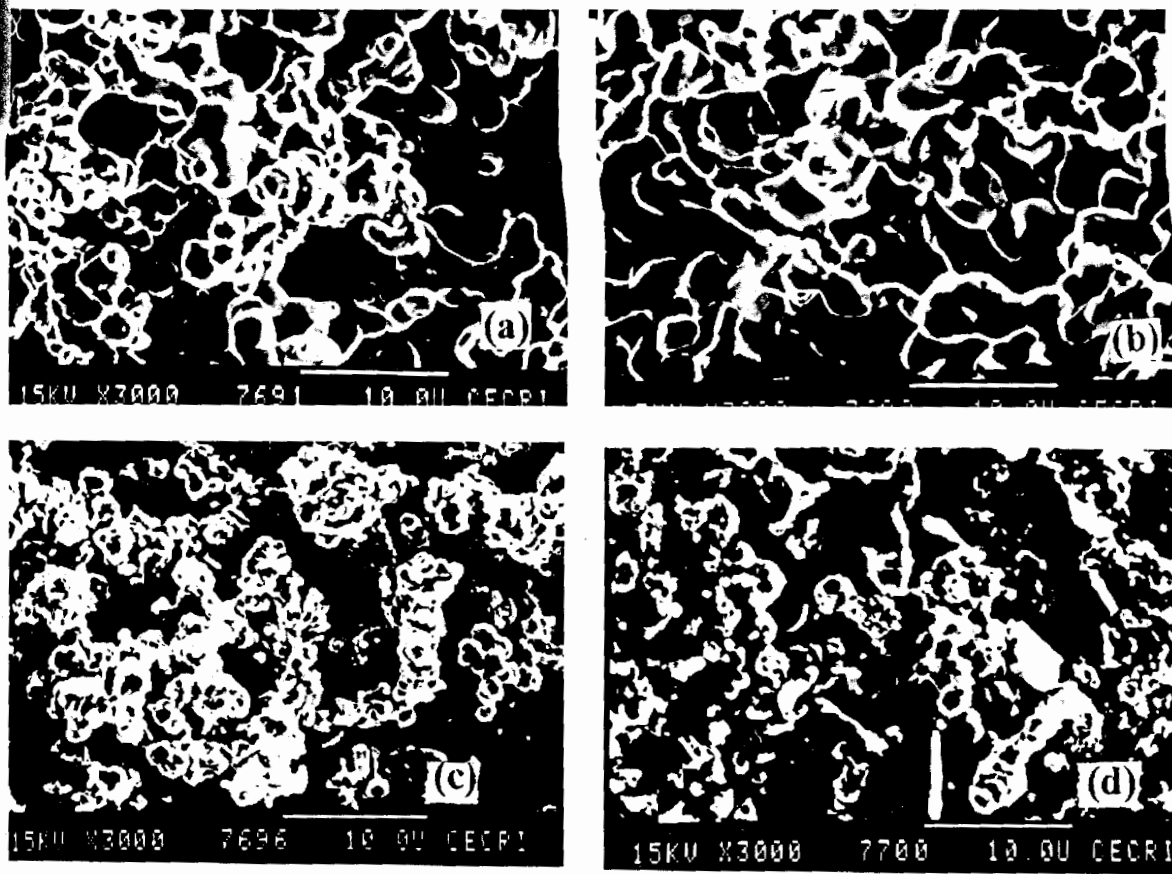


Fig. 4—SEM photo micrographs of (a) loose powder sintered Ni compact, (b) tape cast and sintered electrode, (c) electrode (a) after in situ lithiation and (d) electrode (b) after in situ lithiation

Results and Discussions

The TGA study (Fig. 1) of the system Ni+Li₂CO₃ indicated that the decomposition of Li₂CO₃ is initiated by Ni and starts much earlier 500°C compared to 700°C for the pure salt. In a similar fashion, the oxidation of Ni is also taking place from 500°C. A monotonous weight increase is observed till 700°C. The weight increase can be explained as to the formation of Li_xNi_{1-x}O solid solution due to the co-existence of the two processes viz. Ni oxidation and Li₂CO₃ decomposition²⁴. Beyond 700°C, the weight decreases due to Li₂O loss from the solid phase. It is suggested that the best way to obtain prelithiated nickel catalysts is to start with a mixture of Ni+Li₂CO₃ with a suitable binder (carboxyl-methyl cellulose) and heat it at 550°C for 50 h or at 650°C for

the physical characteristics of the lithiated nickel samples prepared by ex-situ method are listed in Table 1. In all the five batches of lithiated oxide powder, the average particle diameter

ranged from 5 – 100 μm, however when the particle size distribution function was analyzed as a function of particle diameter, more than 80% of the particles were in the range of 5 – 30 μm.

From the above table it is seen that substitution of Ni ions by Li ions in a NiO lattice leads to a decrease in the lattice constant values. It has been established that a linear relationship exists between the lithium content and the lattice constant of the mixed oxide²⁶.

Physical characteristics of the green and sintered electrodes

The density values of the loose powder sintered and tape cast Ni electrodes prepared from both hydrogen treated and untreated Ni powder are compared in Table 2. The sinter density values of loose powder sintered electrodes prepared from hydrogen treated Ni powder were found to be higher than those prepared with the untreated powder. Higher sintering temperatures result in lower porosity values. Increase of sintering time beyond 30-60 min

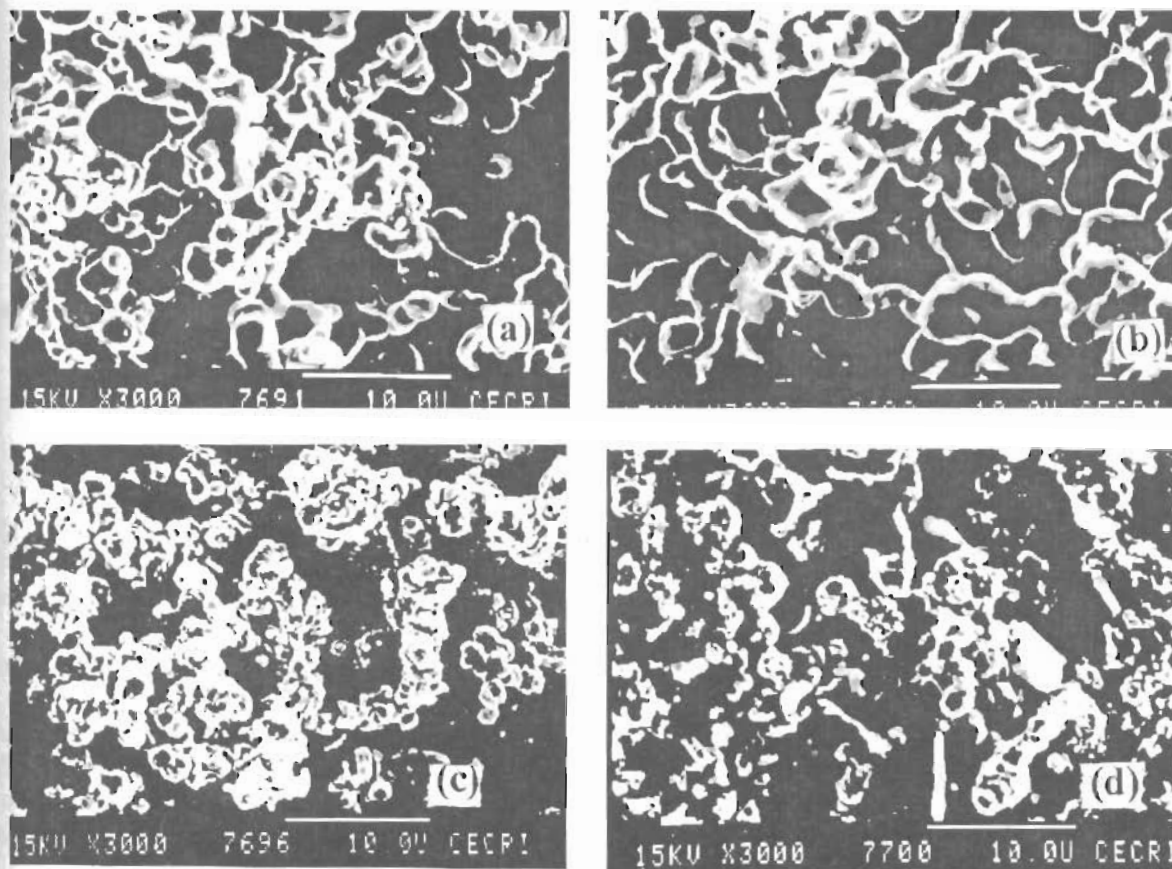


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Results and Discussions

The TGA study (Fig. 1) of the system Ni+Li₂CO₃ has indicated that the decomposition of Li₂CO₃ is accelerated by Ni and starts much earlier 500°C compared to 700°C for the pure salt. In a similar fashion, the oxidation of Ni is also taking place from 240°C. A monotonous weight increase is observed till 700°C. The weight increase can be explained as to the formation of Li_xNi_{1-x}O solid solution due to coexistence of the two processes viz. Ni oxidation and Li₂CO₃ decomposition²⁴. Beyond 700°C, the weight decreases due to Li₂O loss from the solid phase. It is reported that the best way to obtain prelithiated nickel oxide catalysts is to start with a mixture of Ni+Li₂CO₃ along with a suitable binder (carboxyl-methyl cellulose) and heat it at 550°C for 50 h or at 650°C for 5 h²⁵.

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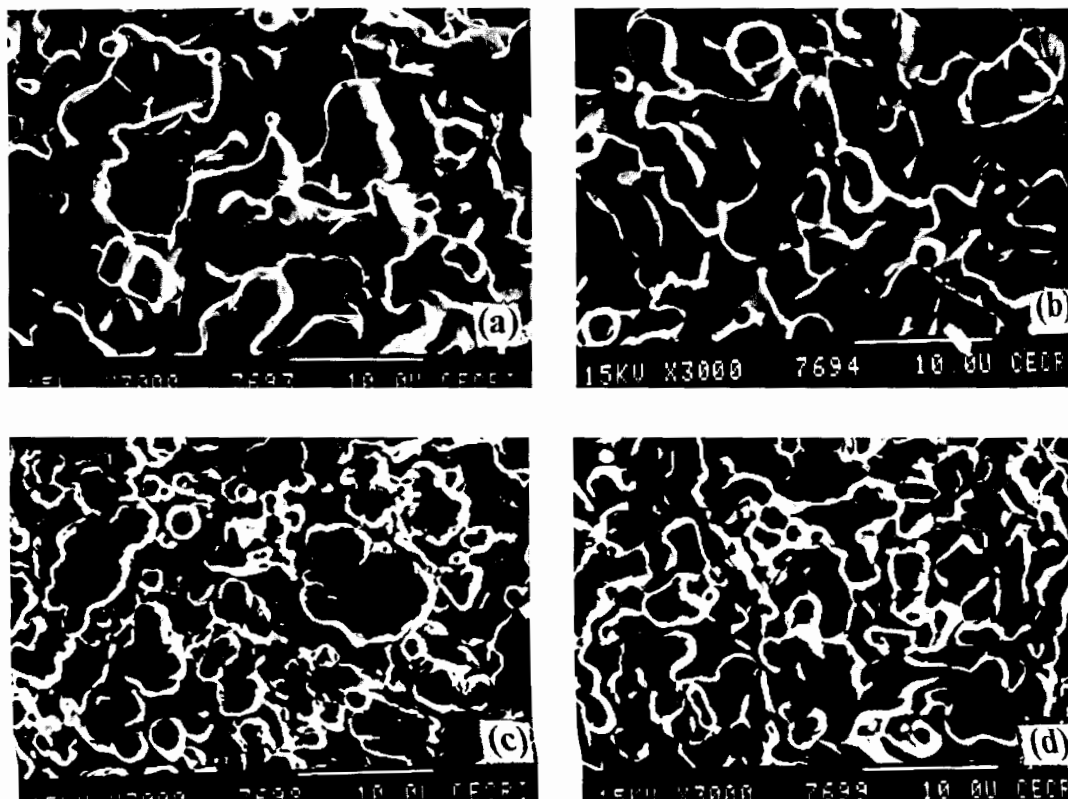


Fig. 5—SEM photo micrographs of (a) Ni + pre-oxidised LiNiO tape (b) Green tape of prelithiated Ni electrode (c) same in-situ oxidised cathode, (c) same ex-situ oxidised and sintered

may not have much influence on porosity. But both of them were reported to influence the strength of the sintered electrode²⁷. Improved strength and conductivity accompany a decrease in porosity as a consequence of the increase in bond area formed between particles. These sintering conditions become vital in achieving optimum electrode porosity.

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 component²⁸. Slurry casting method has been developed and reported in literature using polyvinyl alcohol or methylcellulose as binder²⁹. To obtain a fast curing method a non-aqueous process has also been reported³⁰. The parameters influencing the tape casting of nickel powder by an aqueous slurry process have been investigated³¹. Tape casting with aqueous slurries has several advantages over non-aqueous method in that the former involves handling of nontoxic materials and vapours³². 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 evaluated by TGA study. The TGA and DTA of the green nickel tapes determine the sintering conditions. A typical DTA/TGA curve of the nickel tape is shown in Fig. 2. Initially, the steady weight loss up to 110°C indicating the binder from the green tape is removed. On further heating secondary weight loss is noticed up to 350°C indicating the plasticizer and binder material removed. Nickel starts oxidising at temperature 400°C in air. This is useful in determining the temperature profile during the sintering stage.

Consequently the electrodes are sintered in air atmosphere at a slow heating rate of 1°C/min with intermittent soaking stages at 150°C for 3 h and 350°C for 3 h to remove the inorganic and organic constituents. The final sintering temperature was 800°C for one hour and the product is cooled to room temperature at 1°C/min.

Table 2 also indicates the characteristics of the green tapes and the sintered electrodes prepared from the tapes after controlled sintering. Both the shrinkage factors, density values of the green and sintered tapes and the final porosity values are reported.

Table 3--Cell Voltage - Current density characteristics of different Cathodes

Electrode No.	O. C. V. (V)	Cell voltage (V)	Current (A)	C. D. (mA/cm ²)	Test hours (h)
<i>In situ lithiated Ni electrodes</i>					
8.	0.942	0.644	1.32	29.3	120
6.	0.961	0.721	1.75	39.0	135
<i>Pre lithiated, tape cast and out of cell sintered Ni electrodes</i>					
9.	0.935	0.620	7.40	164	375
10.	0.953	0.633	7.62	170	500
12.	0.966	0.632	7.27	162	530
<i>Pre lithiated, tape cast and in cell sintered Ni electrodes</i>					
13.	0.891	0.632	1.63	36.3	120
14.	0.995	0.600	3.00	66.6	200
15.	0.899	0.631	4.05	90.1	200

the green compact depends upon the binder (t.), slurry composition, solvent (water) plasticizer amount and casting rate³³.

Figure 3 shows the total current and the current densities from carbonate fuel cells with different structures described above. A maximum current density of 40 mA/cm² was obtained with in-situ oxidised and lithiated cathodes. The major advantage of in-situ oxidised cathodes is the volume stability during oxidation and lithiation leading to a weak electrode¹³. The lower performance of in-situ oxidised cathodes can be explained due to the loss of electrolyte from the matrix. The cathode stability is also reported to be important to have low over-polarisation³⁴. Electrodes with uniform porosity and desired porosity can be achieved by the tape casting method.

The size distribution pattern for a typical electrode (Electrode no. 8 of Table 2) is indicated in Figure 4. This figure indicates that an electrode with a porosity of 75%, the average pore size is around 8.5 microns, which is more suitable for a cathode. The total penetration volume (TPV), the average pore dia, the total pore porosity values for the sintered electrodes are related to the performance as cathodes. The electrodes with higher porosity have higher penetration and higher internal pore area (>5 m²/g). It is reported that INCO Ni-255 is good for the preparation of the cathodes with porosity in the range of 70-80% with a mean pore size of 7-9- μ m¹³.

Ex-situ cathodes were prepared by using the method described in Table 1 (pre-lithiated and in-situ), their in-cell performance was lower than in-situ cathodes. It is reported that as NiO

content increases in a mixture of Ni+NiO both the cathode microporosity and the mean pore dia decreases⁴. Hence, the lithiation was restricted to only between 2 and 3 atom % in the preparation of further catalysts. However, when pre-lithiated Ni was used as green tape and oxidised in-situ, the current density values increased above 60 mA/cm². The state of art current density values could not be realised with the in-cell oxidation of pre lithiated electrodes. The lower performance can be attributed to micro structural changes of the cathode during in cell oxidation. Moreover these electrodes had poor strength and were easily fragile since NiO requires higher sintering temperature (>800°C), which is not possible at the cell operating temperature (650°C). Use of green tape, as cathode requires reinforcement to the structure. SS fibers were used while preparing the green tapes by the tape casting method. This not only increased the mechanical strength, but also increased the thickness of the electrodes. Both of them will indirectly affect the total porosity and microstructure of the cathode.

Hence the procedure was modified in such a manner that both the oxidation and sintering of pre-lithiated nickel tapes was done out side the cell in a programmed manner. This has resulted in a better control over the porosity and pore structure of the electrodes. These pre-sintered cathodes exhibited a performance value of 160 mA/cm² and the cells were also tested for duration exceeding 500 h.

SEM results

The scanning electron microscopy can help to relate the microporosity changes and particle morphology accompanying the preparation of cathodes by both in-situ and ex-situ methods. Fig. 4

shows the micrographs of the sintered electrodes prepared by both loose powder sintering and tape casting methods and their characteristics after testing in carbonate cells at 650°C (In-situ lithiation). In cell lithiation and oxidation reduces the intergranular voids affecting the cathode microporosity.

Fig. 5 shows the micrographs of the pre-lithiated tapes. Particle coarsening due to oxidation reaction of Ni to NiO was noticed (Fig. 5c). Uniform pore size was observed with pre-sintered cathodes (Fig. 5d), similar to Fig. 4b. These electrodes have resulted in optimum performance of 160 mA/cm². The particles are well sintered when ex-situ sintering was carried out.

Conclusion

The electrodes were prepared either by loose powder sintering or by tape casting methods. These electrodes were lithiated in-situ inside the cell. Pre-lithiated nickel oxide powders were tape cast either as such or after external oxidation. But the latter method was found to result in lower porosity values. The tapes prepared from pre-lithiated powder were used in the molten carbonate fuel cell as cathodes after external oxidation and sintering. This had resulted in better performance of the cells than while employing green tapes and sintered under insitu condition.

Acknowledgement

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