

## A new way of obtaining $\text{Li}_x\text{Ni}_{1-x}\text{O}$ cathodes for molten-carbonate fuel cells

Ermete Antolini

Ansaldo Ricerche, Corso Perrone 25, 16161 Genoa (Italy)

(Received March 23, 1992; in revised form May 27, 1992)

### Abstract

An unsintered nickel plaque containing  $\text{Li}_2\text{CO}_3$  and an organic binder were tested as a cathode in a molten-carbonate fuel cell. Organic burnout, nickel oxidation, lithium carbonate decomposition and  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  solid-solution formation occurred during the start-up of the cell. The in-cell test showed good performance after a short time of operation, and a limited performance decay after 3500 h.

### Introduction

The state-of-the-art molten-carbonate fuel cell (MCFC) uses a lithium-doped porous nickel oxide cathode which provides an electrical path for the transport of electrons to the electrolyte. In addition, the cathode allows for passage of carbon dioxide and oxygen reactants to the electrolyte via the open pores, and catalyzes the subsequent formation of carbonate ions [1].

Lithiated nickel oxide cathodes can be fabricated in several ways:

(i) The fuel cell can be assembled with a porous metallic nickel cathode in the form of a plaque, which becomes oxidized and lithiated *in situ* soon after the cell is brought to operating temperature. The lithium is supplied by the electrolyte, the oxygen by the gas phase.

(ii) The nickel plaque can be oxidized, or oxidized and lithiated before it is assembled into a cell.

(iii) The cathode can be fabricated directly from nickel oxide powder and incorporated into the cell as a porous sintered ceramic. The oxide powder can be lithiated either before the structure is formed, during sintering, or the cathode can be lithiated in the cell.

(iv) Metallic nickel powder can be sintered in air so that oxidation and sintering occur in one process.

*In situ* oxidation is the method commonly used to obtain MCFC cathodes. A number of problems are associated with the *in situ* oxidation of a sintered nickel structure. The *in situ* oxidation of the nickel plaque causes the original nickel microstructure to break into clusters of much smaller particles with no interconnections, leading to a cathode that is structurally weak and friable [2]. Another problem is a 30 to 40% volume expansion during the oxidation and lithiation of the nickel. This swelling has been troublesome in test cells and may be a severe problem in a stack of hundreds of cells. During *in situ* oxidation the lithium for doping is supplied by the  $\text{Li}_2\text{CO}_3\text{--K}_2\text{CO}_3$  electrolyte, resulting in an early consumption and compositional

variation of the electrolyte and possibly a less than optimal lithium concentration in the final product. Additionally, the sintered nickel structure that is oxidized is expensive.

Because of these problems, several research groups have explored the use of preformed NiO cathodes [3–6]. At the Energy Research Corporation (ERC) the first *ex situ* fabrication procedure resulted in fairly brittle, prelithiated oxide cathodes [7]. Although substantial improvements in strength and electronic conductivity had been achieved with the preformed NiO cathodes, their in-cell performances were frequently lower than the typical state-of-art *in situ* cathodes. The lower performances of preformed cathodes have been attributed primarily to non-optimized microstructures – the improvement of strength by NiO sintering decreases the microporosity below the level needed for optimal performance –. During *in situ* oxidation the nickel particles break up into agglomerates of smaller NiO particles. The pore-size distribution becomes broader, with submicron pores within the NiO agglomerates and large pores between the agglomerates. Such a pore distribution seems best suited for high cathode performance.

In an attempt to overcome the problems of *in situ* cathode formation and to retain optimum structure, in our laboratory a new way of obtaining MCFC cathodes was tested. A green tape consisting of metallic nickel powder, lithium carbonate powder and carboxymethylcellulose as the binder was assembled in the cell [8]. The application of an unsintered plaque (green) in a MCFC cell was also tested by Kaun *et al.* [9], but they used NiO as starting powder. This plaque requires sintering in the temperature range 650 to 750 °C, which is very high temperature for the MCFC. The results of the related in-cell test were not reported.

This paper describes work at Ansaldo on the application of unsintered nickel plaques for *in situ* cathode formation, the advantages of using such cathodes, and the performance of a cell equipped with such a cathode.

## Experimental

### *Cathode preparation*

Nickel (INCO 255), lithium carbonate powder, a binder, and an antifoam agent, were mixed in a polyethylene bottle with de-ionized water. The resulting slurries were degassed and cast onto beewax-coated surfaces. After the castings had dried, 100 mm × 100 mm plaques, with a thickness 0.45 mm, were cut using a razor blade and a template.

Following preparation, the plaques were either used for out-of-cell tests or assembled in MCFC. In Fig. 1 the process flow diagram for cathode preparation is shown.

### *Out-of-cell tests*

The plaques were subjected to the following thermal cycle in air: (i) heating at 3.6 °C/min to 550 °C (650 °C); (ii) isothermal soak for 50 h at 550 °C, or 5 h at 650 °C; (iii) cooling at 1.8 °C/min.

### *In-cell tests*

The tests were carried out at the temperature of 650 °C, with a fuel simulating, a complete methane steam reforming gas and a cathodic gas with an air/CO<sub>2</sub> ratio 70/30. Binder burnout, nickel oxidation, lithium carbonate decomposition and solid-solution formation occurred during the start-up of the cell. The test lasted 3500 h during which the cell was subjected to two shutdowns.

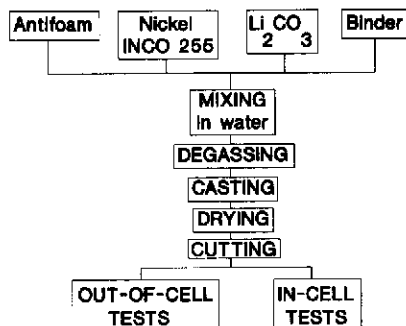


Fig. 1. Processing flow diagram for cathode preparation.

The other components used in the cell were the following:

(i) Anode. The anode structure comprised nickel and nickel-coated ceramic powders. The thickness was 0.5 mm and the overall porosity was about 70%.

(ii) Electrolyte matrix. The electrolyte was the eutectic  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  mixture. The electrolyte matrix consisted of a three-layer sandwich with an overall thickness of 0.9 mm. The 57% porous innerlayer was a  $\gamma\text{-LiAlO}_2$  ceramic structure, sintered at about 950 °C, filled with electrolyte. The extra layers have the function of electrolyte reservoir: they are constituted by an unsintered mixture of  $\gamma\text{-LiAlO}_2$ ,  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  in the eutectic composition and a binder (butvar).

(iii) Current collectors/gas distributors. The current collectors/gas distributors were constituted by a stainless steel AISI 316 gauze, for contact with the electrodes, and by a ribbed sheet of the same material spot welded to the housing.

## Results and discussion

### Out-of-cell tests

Out-of-cell tests were performed to evaluate the volume variation of the plaque following binder burnout, nickel oxidation, carbonate decomposition and solid-solution formation.

Isothermal treatments in air at 550 °C for 50 h or at 650 °C for 5 h were enough to obtain the complete nickel oxidation,  $\text{Li}_2\text{CO}_3$  decomposition and solid-solution formation. These reactions simultaneously occurred starting from 240 °C, as indicated in ref. 10. Nickel-catalyzed  $\text{Li}_2\text{CO}_3$  decomposition at temperatures lower than the spontaneous  $\text{Li}_2\text{CO}_3$  decomposition temperature [10], allowed for solid-solution formation of lithium ions in intimate contact with the nickel grains, without electrolyte consumption.

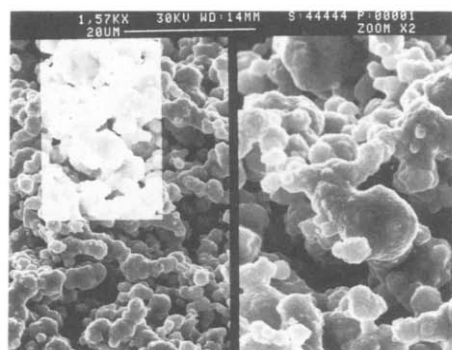
As can be seen in Table 1, the sample containing 6 at.%  $\text{Li}^+$  showed a negligible volume variation of the plaque: this behaviour results from the opposing effects of the shrinkage due to the rearrangement of nickel grains following binder burnout and the volume expansion due to carbon dioxide release from  $\text{Li}_2\text{CO}_3$  decomposition. Therefore, the composition with 6 at.%  $\text{Li}^+$  was used for the preparation of the cathode.

The structural morphology of the plaque following out-of-cell thermal treatment at 600 °C for 10 h and following 100 h of cell operation is shown in Fig. 2(a) and 2(b), respectively: the multigranular structure of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  particles is visible in both

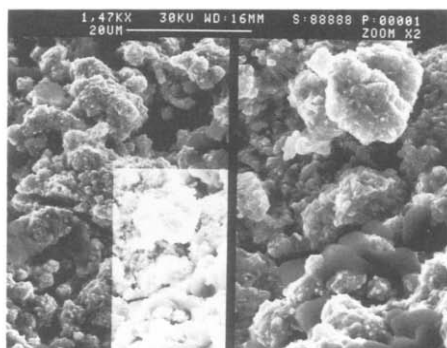
TABLE 1

Volume variation of the plaque (as determined with following thermal treatment of nickel plaques containing different amounts of lithium carbonate)

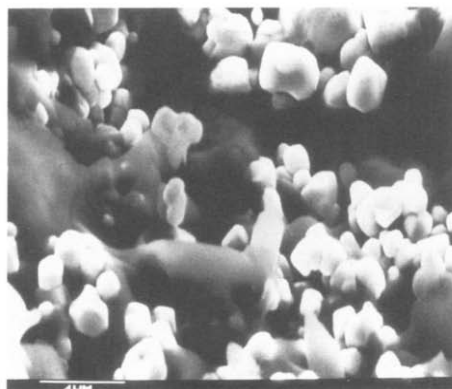
Plaque composition (at.% Li <sup>+</sup> )	Thermal treatment	
	550 °C/50 h	650 °C/5 h
	volume variation (%)	
0	-3.5	-3.6
6	0.2	0.4
10	2.0	4.6



(a)



(b)



(c)

Fig. 2. Scanning electron micrographs of porous lithium-doped nickel oxide cathode following (a) out-of-cell thermal treatment at 650 °C for 10 h (1570× magnification (200 m double magnification)), (b) in-cell test for 100 h (1470× magnification (200 m double magnification)), and (c) in-cell test for 3500 h (5400× magnification).

the samples. In Fig. 2(c), the SEM image of the cathode after 3500 h is shown: morphological changes compared to Fig. 2(b) (break of the agglomerates and disappearance of the intragranular voids) are evident, according to Minh [1], who reports a change of the cathodic microstructure during cell operation, and Maru *et al.* [11], who report an extensive coarsening of the material as a result of dissolution/precipitation reactions, giving rise to surface-area decay.

The cathodic material being unsintered, a structurally weak and friable electrode should be expected; instead, by handling, all the samples showed a good strength (confirmed by the inspection of the electrode following in-cell test), similar to that of conventional NiO cathodes.

### *In-cell performance*

Figures 3 and 4 show the current density versus time at constant voltage (750 mV) and the voltage/current characteristics after 3400 h, respectively. Two shutdowns at 1400 h and 3050 h were necessary to remove carbon deposits due to problems arisen in the humidification system. The cell exhibited good performance at the beginning of the test (190 mA/cm<sup>2</sup>). The decrease in the cell performance was limited to 18% after 3500 h. The main cause of current density decay was the electrolyte loss: enough electrolyte must be available to allow ionic conduction and to prevent gas cross-over through the matrix. Insufficient ionic conduction causes high cell resistance, so it follows that cell performance is lowered by an increase of internal resistance drop. Gas cross-over through the matrix causes a decrease in concentration of reactant gases and results in cell performance decay.

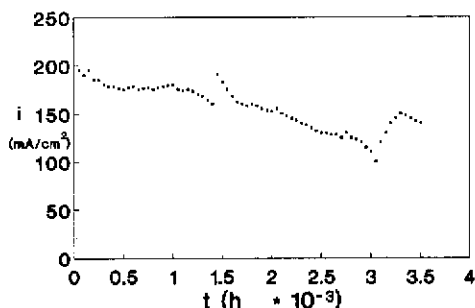


Fig. 3. Cell current density at constant voltage (750 mV) measured during the test.

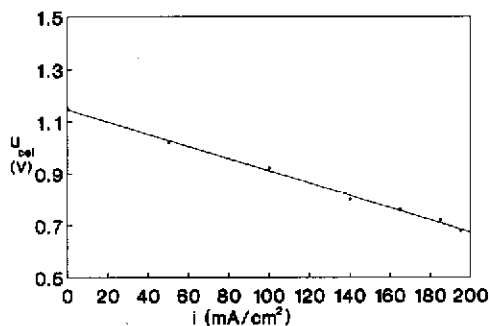


Fig. 4. Cell voltage/current density characteristic after 3400 h.

A test carried out in the same experimental conditions, which is still in progress on a new cell, shows better performances, such as a current density of 230 mA/cm<sup>2</sup> at 750 mV after 800 h. In this cell, we have decreased the thickness of the matrix and optimized the electrolyte amount.

The same component technology was used by Ansaldo for the realization of a stack of ten 300 mm×300 mm cells that supplied 650 W at atmospheric pressure.

Promising tests are in progress using an unsintered cathode and an unsintered matrix tape, and putting the electrolyte in the anode.

## Conclusions

The use of an unsintered nickel plaque containing Li<sub>2</sub>CO<sub>3</sub> as MCFC cathode combines the advantages of *in situ* oxidation and lithiation of metallic nickel plaque, and the use of preformed NiO plaque:

- (i) *in situ* oxidation leads to a pore distribution desirable for high cathode performance;
- (ii) no volume expansion occurs;
- (iii) good strength of the cathode was found following the endurance test;
- (iv) no electrolyte consumption occurred;
- (v) presintering of the plaque (expensive process) is not needed;
- (vi) good cell performance seems obtainable.

## Acknowledgement

The author thanks Dr M. Scagliotti, Cise, for SEM images of the samples following in-cell test for 3500 h.

## References

- 1 N. Q. Minh, *J. Power Sources*, 24 (1988) 1.
- 2 R. D. Pierce, P. A. Finn and R. B. Poeppel, *Proc. Symp. Molten-Carbonate Fuel Cells, Montreal, May 9-14, 1982*, The Electrochemical Society, Pennington, NJ.
- 3 R. D. Pierce, J. L. Smith and R. B. Poeppel, *Advanced Fuel Cell Development, Report No ANL-81-68 for DOE Contr. W-31109-Eng-38*, Argonne National Laboratory, Argonne, IL, 1981.
- 4 *Advanced Technology Fuel Cell Program, Final Report EM-1730 for EPRI Research Project RP114*, United Technologies Corporation, South Windsor, CT, 1981.
- 5 *Development of Molten Carbonate Fuel Cell Powerplant, Quarterly Report No 17019-6 for DOE Contr. DE-AC02-80ET17019*, General Electric Company, Schenectady, NY, 1981.
- 6 E. Antolini, M. Leonini, V. Massarotti, A. Marini, V. Berbenni and D. Capsoni, *Solid State Ionics*, 39 (1990) 251.
- 7 A. Pigeaud, *Development of Molten Carbonate Fuel Cell Technology, Report No CHI/11304-19 for DOE Contr. DE-AC03-76ET11304*, ERC, Danbury, CT, 1980.
- 8 E. Antolini, *European Patent, No 91 108 138.8* (1991).
- 9 T. D. Kaun and F. C. Mrazec, *US Patent 4 891 280* (1990).
- 10 A. Marini, V. Berbenni, V. Massarotti, G. Flor, R. Riccardi and M. Leonini, *Solid State Ionics*, 32/33 (1989) 398.
- 11 A. Pigeaud, H. C. Maru, L. Paesch, J. Doyon and R. Bernard, in H. C. Maru (ed.), *Proc. Symp. Porous Electrodes: Theory and Practice*, The Electrochemical Society, Pennington, NJ, 1984, p. 234.