

## Endurance test on a single cell of a novel cathode material for MCFC

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### Abstract

The molten carbonate fuel cell (MCFC) is expected to be an efficient device for the conversion of chemical energy in the near future. However, one of the major limits to the lifetime is the dissolution of the nickel oxide cathode in the electrolyte. This problem can be overcome by the addition of new compounds to the nickel oxide. In this way, the performance and the endurance of a new Ni–Ce cathode for MCFC has been tested and the results compared to a commercial nickel cathode. The polarisation curves were measured in order to check the degradation of the cell performance with time. The results showed a better performance with the novel cathode material (136 mW/cm<sup>2</sup> at 200 mA/cm<sup>2</sup> during 2100 h) than the commercial one (the voltage decreased from 120 to 108 mW/cm<sup>2</sup> at 150 mA/cm<sup>2</sup> in 1000 h). The better performance of Ni–Ce cathode with respect to the Ni one can be attributed to the good effect of cerium in the cathode. The change in the nickel crystalline structure reduces the dissolution of nickel in the electrolyte and implies a greater endurance of the cell. The current–voltage curves were measured and showed the same trend for both cells. Postmortem analyses were done in order to characterise the cells. As a conclusion, the addition of cerium can be beneficial to overcome the dissolution of the nickel cathode in the electrolyte, which is considered one of the major limits to the lifetime of a MCFC. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Molten carbonate fuel cell; Cathode; Nickel oxide; Corrosion; Cerium oxide

### 1. Introduction

Fuel cells may be expected, in the long term, to replace a major part of combustion systems in all end use sectors, where they are, intrinsically clean [1]. One of the most promising electric power generation systems currently being sponsored by the US Department of Energy's National Energy Technology Laboratory is the molten carbonate fuel cell (MCFC) [2]. After having been under study and development for more than 40 years, MCFC are approaching the early stages of commercialisation [3–5]. In fact, the start-up, testing and operation have been carried out in several pilot plants [6–9].

Nickel oxide is commonly used as the cathode material for the molten carbonate fuel cells because of its high activity and conductivity in the operation conditions. However, one of the major limits to the lifetime is the dissolution of the nickel oxide in the electrolyte resulting in a degradation of cathode performance [10]. There is also a risk that dissolved nickel precipitates in the matrix on the anode side

and causes a short-circuit of the cell. Attempts were made to solve this problem by looking for other materials. Previous work on LiFeO<sub>2</sub>, Li<sub>2</sub>MnO<sub>3</sub> and LiCoO<sub>2</sub> cathodes showed that electrodes made with these were very stable chemically in the cathode environment because of the low dissolution rate [11–15]. However, the electronic conductivity was lower than that of NiO [16,17]. Recently, new candidate materials such as LiCoO<sub>2</sub>-coated NiO [18] and pre-oxidised nickel–niobium surface alloy [19] have been proposed.

The most promising way to modify the properties of nickel oxide in the desired direction was, in our opinion, the incorporation of cerium cations into the nickel oxide. Cerium oxide is actually being used, as promoter, in many three way catalyst formulations, incorporated in car exhausts to control polluting emissions. The presence of cerium stabilises the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support against transformation to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, acts as an oxygen storage, helps to maintain the active metal dispersion under working conditions and produces a good electrical contact between oxides, that facilitates electron transfer between cerium oxide and the supported metal oxide. In this work, cerium oxide has been incorporated into a cathode based on nickel oxide and the performance and endurance has been compared with that of a commercial NiO cathode.

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Fig. 1. Photograph of the experimental device during the operation.

## 2. Experimental

### 2.1. Experimental system

Fig. 1 presents the experimental system where tests were carried out. It consists of a set of mass flow controllers to feed the reactant gases to both the anodic and cathodic sides. The mixtures of gases pass through humidifiers, which are filled by means of a peristaltic pump. The gases continue along a heated pipe to the electric pre-heaters where the temperature is increased. Then, they are injected to the fuel cell, which is heated by an external electrical furnace with a PID controller. The cell is shut with a piston driven by compressed air. Finally, the water from the exhausted gases is condensed before being removed. The control and the data acquisition are made by means of specific PC software.

The cell was circular in shape and the dimension was 50 mm diameter. The material used in housings was 316 stainless steel and, it was coated with aluminium by a plasma deposition treatment. Cathode, anode and current collectors were 32 mm diameter.

For the load demand dc electronic load (Hewlett Packard 6060B) was used. The gas composition inlet and outlet for anodic and cathodic lines were measured by means of a gas chromatograph (Varian 3800 with molecular sieve 13X 60/

80 and Porapak Q 80/100 columns) and the internal resistance with a HP 1142A probe control connected to a Tektronix TDS3012 oscilloscope.

The structure of the samples was characterised before and after the electrochemical tests by scanning electron microscopy (SEM) using a Hitachi S-2500 and the distribution of the aluminium, iron and nickel in the components of the cell after operation by EDX.

### 2.2. Components

The anode used was a commercial material which consists of a mixture 98% Ni–2% Cr. The porosity was 61–63% and the pore mean diameter 2–5  $\mu\text{m}$ . The anode was prefilled with electrolyte (0.05  $\text{g}/\text{cm}^2$ ). The electrolyte support was made of  $\gamma\text{-LiAlO}_2$ . The porosity was 50–55% and the pore mean diameter 0.1–0.5  $\mu\text{m}$ . The cathodic current collector was stainless steel and the anodic current collector was stainless steel protected with nickel.

The electrolyte consists of a 62  $\text{Li}_2\text{CO}_3$ /38  $\text{K}_2\text{CO}_3$  eutectic presented in sheets. Calculation of the quantity of electrolyte that must be added to the cell was carried out taking into account the relative percentage of carbonates. The optimum percentage of filling was taken from other work [20].

Table 1  
Textural characteristics of the cathodes used

Cathode	Porosity (%)	Pore mean diameter ( $\mu\text{m}$ )
Ni–Ce	71.7	7.1
Ni	74–78	3–6

The commercial cathode was prepared with nickel using the tape casting technique. As the preparation of nickel cathodes is a well established process and we wanted to maintain the optimised textural properties of the commercial cathodes, we have used a similar preparation method, only slightly modified to accommodate the differences introduced by cerium incorporation. Metallic nickel powder was impregnated with cerium nitrate and dried at 70 °C under vacuum. This precursor was treated at 500 °C for 3 h under nitrogen and, again, at 500 °C for 1 h under a reducing gas mixture ( $\text{N}_2:\text{H}_2 = 1:1$ ). The sintering process was carried out under a reducing gas mixture ( $\text{N}_2:\text{H}_2 = 25:1$ ) in two steps: the first step to give form to the cathode at temperatures in the 700–900 °C range, and the second, for densification, in the 1000–1200 °C range. Considering that the presence of  $\text{CeO}_2$  would hinder the sintering process, the sintering temperatures were increase with the cerium content. Previous work showed that the composition 0.5% Ce provided the minimum corrosion rate for the cathode after measuring nickel oxide dissolution rate in the molten carbonate mixture [21]. All the prepared samples were studied by XRD and SEM and their surface area and porosimetry were measured, to check if these parameters were appropriate for this study. The comparative characteristics of both cathodes (Ni and Ni–Ce) are presented in Table 1. The porosity for the Ni–Ce is slightly lower but the pore mean diameter is bigger than that of the commercial nickel cathode.

The morphology can be viewed by means of the SEM technique. From Fig. 2, it is evident that the cerium-impregnated cathode (Ni–Ce) has the same morphology as the Ni cathode.

### 2.3. Operation conditions

A pressure of 2  $\text{kg}/\text{cm}^2$  was applied to the cell by means of a pneumatic piston. The heating rate was 0.5 °C/min, maintaining the temperature at 190, 290 and 470 °C during 4, 7 and 10 h, respectively, under nitrogen in order to achieve a correct removal of organic compounds from the electrolytic support.

Once the operation temperature (650 °C) was achieved the mixtures of gases were fed with flow rates that, theoretically, enable a current density of 300  $\text{mA}/\text{cm}^2$  with a voltage of 0.6 V. Initially, the gas compositions were  $\text{N}_2$  (33 ml/min),  $\text{H}_2$  (40 ml/min) and  $\text{CO}_2$  (27 ml/min) saturated with water at 65 °C as anodic feed and  $\text{N}_2$  (20 ml/min),  $\text{O}_2$

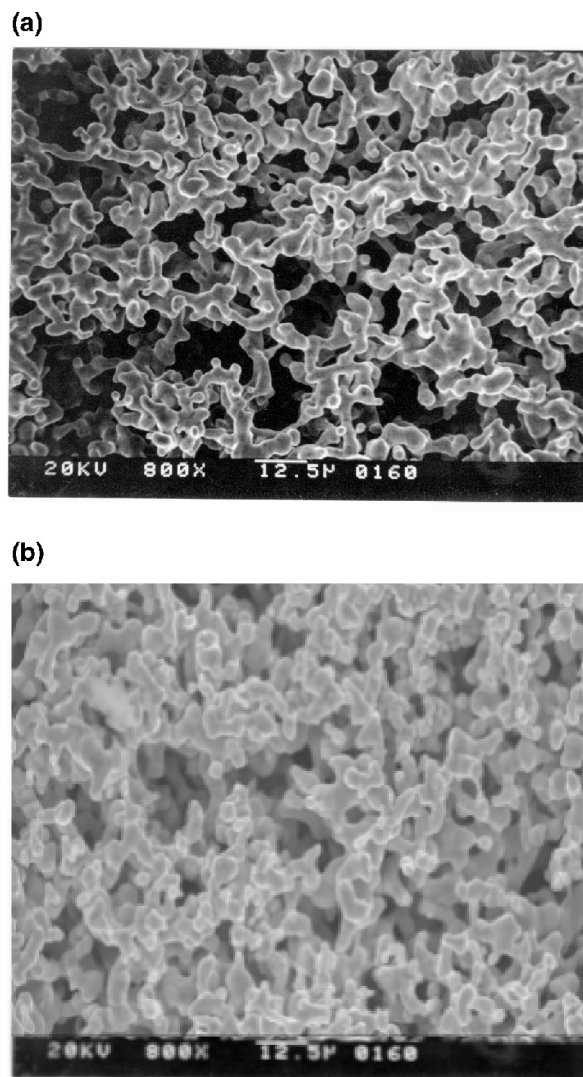


Fig. 2. Cathode morphology after sintering: (a) Ni cathode; (b) Ni–Ce cathode.

(20 ml/min) and  $\text{CO}_2$  (40 ml/min) saturated with water at 35 °C as cathodic feed. Nitrogen was supplied to equilibrate the pressures and the presence of  $\text{H}_2\text{O}$  in the cathodic side was an attempt to simulate the possible recirculation of exhaust gases from the anode to feed the cathode. The temperature of the humidifier was calculated to inject a suitable quantity of water in order to avoid the deposition of coke in the anode. Once the cell reached a good performance, an excess of  $\text{CO}_2$  was fed to the cathode side in order to accelerate its degradation while maintaining the same voltage. So, the gas compositions were modified to  $\text{H}_2$  (40 ml/min) and  $\text{CO}_2$  (60 ml/min) saturated with water at 65 °C as anodic feed and  $\text{O}_2$  (20 ml/min) and  $\text{CO}_2$  (60 ml/min) saturated with water at 35 °C as cathodic feed.

In order to determine the endurance of both cathodes the values of current and voltage were automatically monitored during all the operation time. The current load was maintained at 150  $\text{mA}/\text{cm}^2$  for the commercial cathode and

200 mA/cm<sup>2</sup> for the Ni–Ce. Also, as the polarisation curves were measured at different operation times. The internal resistance of the cell and the gas composition were measured at different operation times, too.

### 3. Results and discussion

The cell with the commercial Ni cathode was tested for about 1100 h of hot time (time after electrolyte melting), 1000 h of which were on load. The cell with the Ni–Ce cathode was tested for approximately 2200 h of hot time, 2100 h of which were on load. The evolution of the performance along the operation time is shown in Fig. 3. The voltage of the commercial nickel cathode decreased from 0.8 to 0.72 V at 150 mA/cm<sup>2</sup> from 200 to 1000 h (120–108 mW/cm<sup>2</sup> in power terms). However, the new Ni–Ce cathode showed a highly stable performance with time, maintaining a voltage of nearly 0.68 V at 200 mA/cm<sup>2</sup> from 200 to 2100 h (136 mW/cm<sup>2</sup> in power terms).

The polarisation curves of the operations are shown in Fig. 4. In the case of the commercial nickel cathode (Fig. 4a) we can observe a continuous decrease of the performance with time. However, the polarisation curves for the Ni–Ce cathode (Fig. 4b) maintains more stable values. The comparison at 1000 h of operation (Fig. 5) gives us further evidence of the better performance of the new cathode.

In the operation of the Ni–Ce cathode cell the control of the gas compositions was made by mean of a gas chromatograph. This study was made in order to know the following data: (1) to check the correct introduction of the inlet gases, (2) to calculate the gas utilisation and (3) to know the possible effect of “cross over”. The gas utilisation data are shown in Table 2. The gas utilisation increases with time to reach a value of approximately 60%. On the other hand,

Table 2  
Gas utilisation during time for Ni–Ce cathode

Hot time (h)	Fuel utilisation (%)	Oxidant utilisation (%)
167	27.0	20.0
704	45.9	13.3
1014	62.6	11.8
1560	60.4	13.8

the effect of the crossover was determined and nearly 1% hydrogen was measured in the cathode outlet gas.

In order to obtain internal resistance data the current density was varied continuously between two values by means of the dc electronic load. Then, the voltage is measured. The internal resistance is calculated dividing the voltage by the difference in current. The results were 110 mΩ on the average (880 mΩ cm<sup>2</sup>) for the Ni–Ce cathode and 55 mΩ (440 mΩ cm<sup>2</sup>) for the Ni cathode. This seems to indicate that, in spite of the higher internal resistance of the new cathode, the beneficial effect of cerium to decrease the nickel dissolution rate shielded to obtain a the better performance.

After finishing the operation a study of the used cells was made in order to analyse the dissolution of the nickel. The presence of nickel in the electrolyte that migrated from the cathode was determined by means of the SEM-EDX technique. A cross section of the cell is shown in the Fig. 6. In Fig. 7a comparison between the two single cells is shown for the nickel distribution. The single cell with the commercial nickel cathode (Fig. 7a) shows a great accumulation of nickel in the electrolyte as a consequence of a high dissolution of the cathode. On the other hand, nickel is scarcely detected in the Ni–Ce cathode (Fig. 7b). This means that during the operation with the Ni–Ce cathode less nickel dissolution of the cathode took place a despite the longer

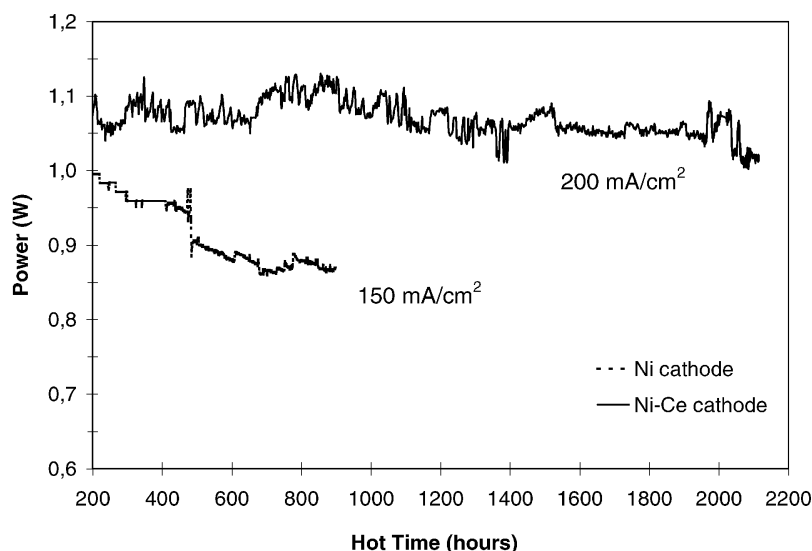


Fig. 3. Performance along the time for both cathodes: Ni cathode at 150 mA/cm<sup>2</sup>; Ni–Ce cathode at 200 mA/cm<sup>2</sup>.

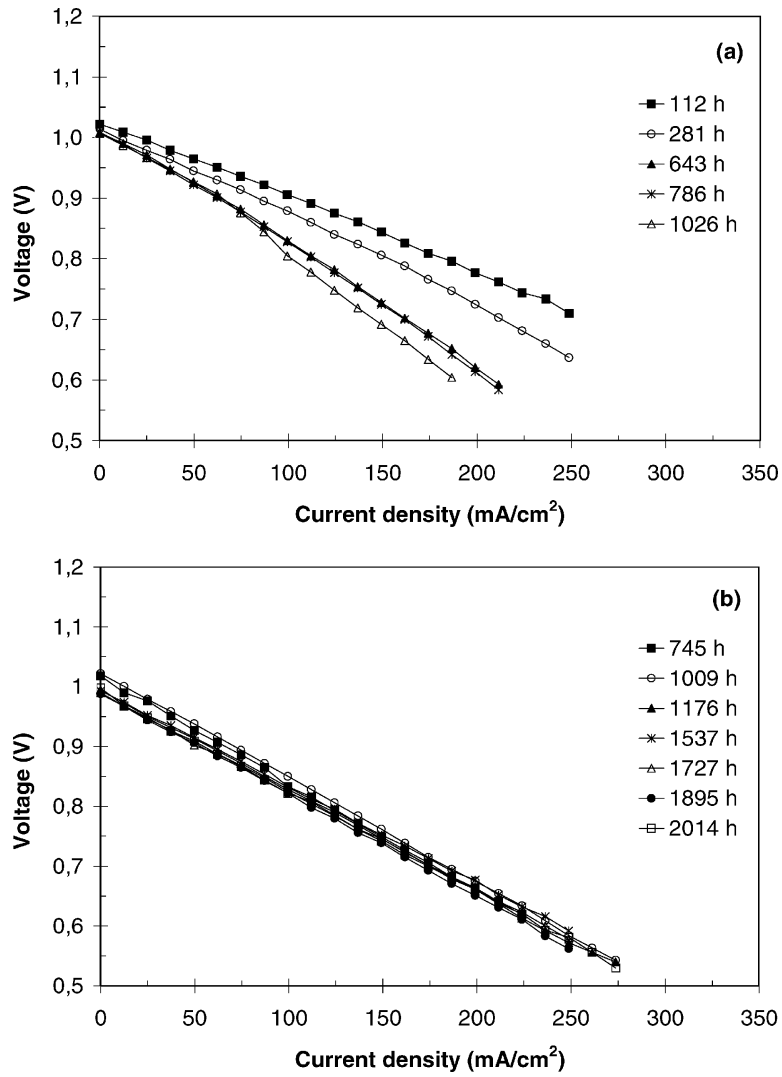


Fig. 4. Polarisation curves along the time for both cathodes. (a) Ni cathode; (b) Ni-Ce cathode.

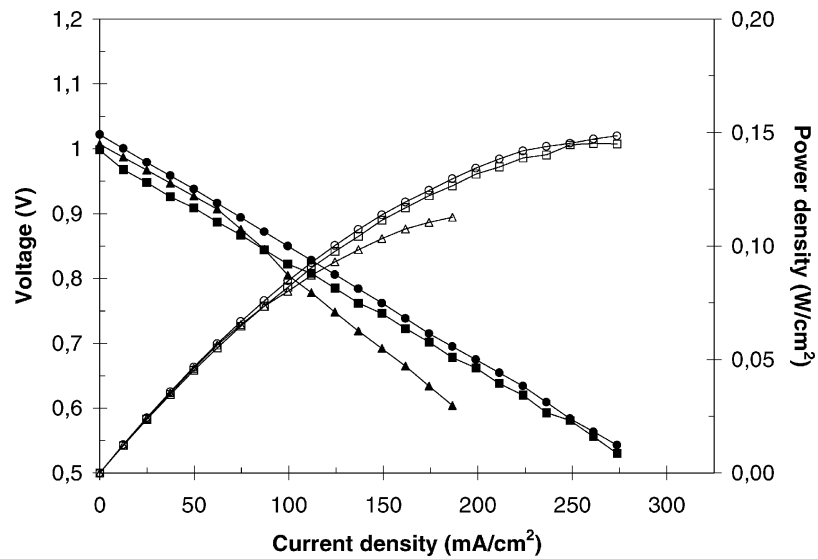


Fig. 5. Comparison of polarisation curves for both cathodes. Solid symbols represent the voltage and the open one the power density. (▲, △) Ni cathode at 1000 h; (■, □) Ni-Ce cathode at 1000 h; (○, ●) Ni-Ce cathode at 2000 h.

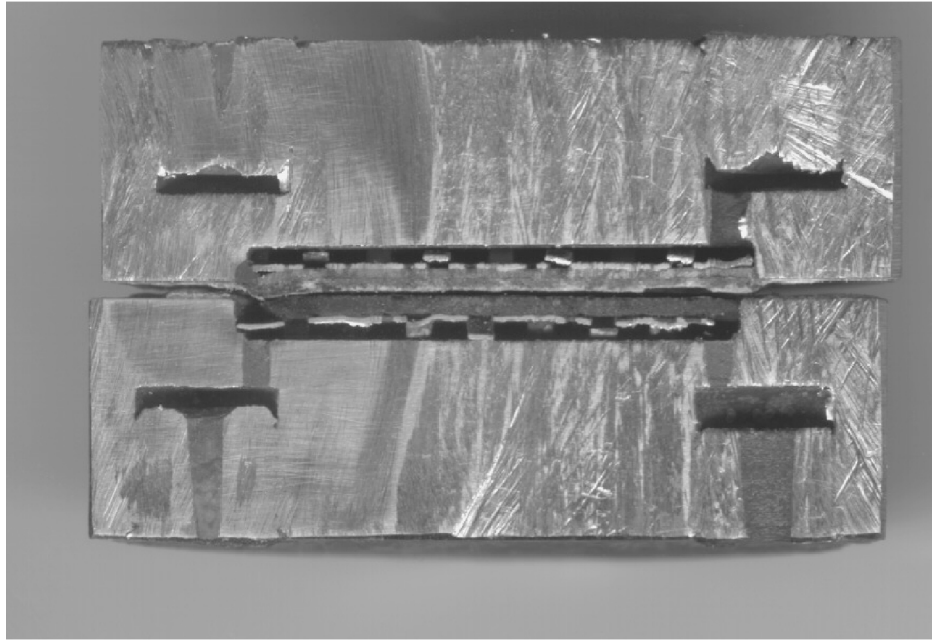


Fig. 6. Cross section of the single cell after the operation.

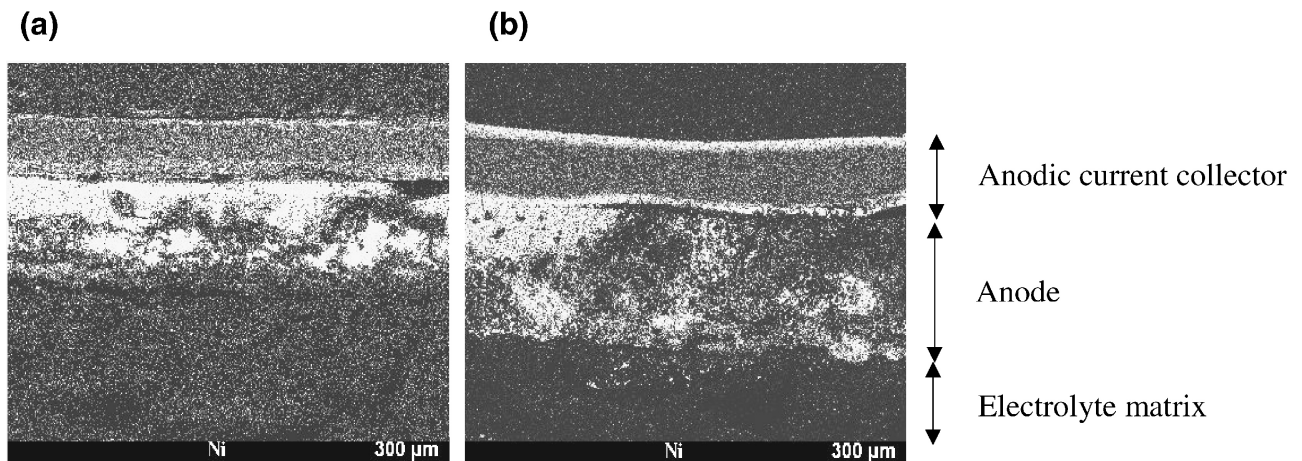


Fig. 7. Comparison of the Ni presence in the cell after the operation: (a) Ni cathode; (b) Ni-Ce cathode.

operating time. Consequently, due to the reduction of the corrosion of the cathode, we can improve the stability and the lifetime of the cell. Also, problems like internal short circuit and low total efficiency of the cell can be minimised.

#### 4. Conclusion

The results of the comparison of new Ni–Ce cathode with a commercial nickel indicate that the addition of cerium results in less dissolution of nickel in the electrolyte and that implies a greater endurance of the cell. The performance of the Ni–Ce cathode was better than that of the nickel commercial and the endurance was more than double. Also, the Ni–Ce cathode was in operation at  $200 \text{ mA/cm}^2$  while the commercial Ni cathode was at  $150 \text{ mA/cm}^2$ . After the

operation a comparative study by means of SEM-EDX techniques showed that a lower quantity of nickel was present in the matrix electrolyte when it operated with the Ni–Ce than with the commercial nickel one. Therefore, cerium incorporation can be used to introduce beneficial effects without damage to the desirable characteristics of nickel oxide as a cathode for MCFC.

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