Modified nickel oxides as cathode materials for MCFC

L. Daza [a,*], C.M. Rangel [b], J. Baranda [a], M.T. Casais [c], M.J. Martínez [c], J.A. Alonso [c]

[a] *Instituto de Catálisis y Petroleoquímica (CSIC)-CIEMAT, Campus UAM-Cantoblanco 28049 Madrid, Spain*
[b] *Instituto Nacional de Engenharia e Tecnologia Industrial Electroquímica de Materiais DM, Paço do Lumiar 22 1649-038 Lisbon, Portugal*
[c] *Instituto de Ciencia de Materiales (CSIC), Campus UAM-Cantoblanco 28049 Madrid, Spain*

Abstract

The preparation and subsequent oxidation of nickel cathodes modified by impregnation with cerium were evaluated by surface and bulk analysis. The cerium impregnated cathodes showed the same pore size distribution curve types and the same morphology as the reference nickel cathode. The measured nickel oxide dissolution rate in the molten carbonate mixture indicated that a minimum corrosion was evident for cathodes with 0.3–1 wt.% cerium oxide content. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed in the cathode characterization. As can be seen by SEM, the corrosion treatments produce marked modifications on the sample surfaces that appear more prominent for the cerium-free sample. The results also show that the lithiation process is a very significant factor that can improve the efficiency of the cell, but needs to be controlled because it can also produce very damaging effects such as the modification of the cathode volume by the formation on new compounds. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

Dissolution of NiO cathodes has led to the search for novel alternative materials that, apart from exhibiting appropriate electronic conductivity and catalytic activity for the oxygen evolution reaction, would also be thermodynamically stable in molten carbonate. The mechanism for the cathodic reaction has also been extensively researched [1–5].

Alternative materials, such as Li–Co–O and Li–Fe–O have been proposed [6]. Modifications in the composition of gas mixtures, varying the partial pressures of CO_2 and O_2 [7], melt composition [7–11], addition of alkaline earth metals to the melt [12], total pressure [14–16] and temperature [9–11,13,14] have also been attempted.

In order to find materials with improved characteristics for cathodes in MCFC, two different methods can be used. The easiest one is to introduce modifications into the best existing materials, in order to modify some of the characteristics that need to improved before use on a commercial scale. In this way, most of the efforts already pursued in many laboratories could be still employed. A second approach is to look for a completely new material. It may be possible to find something better than nickel oxide, but it would take a lot of time just to find some new promising material and to optimize its favorable characteristics.

The most promising way to modify the properties of nickel oxide appeared to be the incorporation of cerium cations to the nickel oxide. Cerium oxide is already being used, as promoter, in many three-way catalyst formulations incorporated to car exhaust to control polluting emissions. The presence of cerium stabilizes the γ-Al_2O_3 support against transformation to α-Al_2O_3, acts as an oxygen buffer, 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.

A novel material has been prepared based on modifying NiO by cerium impregnation. Dissolution of the new material in molten carbonates was evaluated using melt analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The pore size distribution of the cathodes prepared was determined by mercury porosimetry. Taking into account the occurrence of lithiation, some preliminary

* Corresponding author. Tel.: +34-91-585-4786; fax: +34-91-585-4760.
E-mail address: ldaza@icp.csic.es (L. Daza).

Table 1
Textural characteristics of prepared cathodes obtained by mercury porosimetry

Cathode	Porosity (%)	Pore diameter (μm)
Ni	65.75	8.37
NiO	42.14	6.68
Ni–Ce$_{03}$	76.37	8.41
NiO–Ce$_{03}$	63.60	7.34
Ni–Ce$_{05}$	71.74	7.08
NiO–Ce$_{05}$	59.30	6.24
Ni–Ce$_{10}$	75.89	7.71
NiO–Ce$_{10}$	51.44	3.43
Ni–Ce$_{15}$	63.89	7.73
NiO–Ce$_{15}$	60.59	4.12
Ni–Ce$_{50}$	75.19	9.53
NiO–Ce$_{50}$	52.81	8.16

results are presented for ex situ lithiated and cerium impregnated cathodes. Data for NiO are also presented and discussed for comparison.

2. Experimental procedure

The preparation of nickel cathodes is a well-established process. To maintain the optimized textural properties of commercial cathodes, the sintering method was 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. The sintering process was carried out under a reducing gas mixture (N_2:H_2, 25:1) in two steps: the first step to give form to the cathode, and the second, for compaction. Since the presence of CeO_2 would hinder the sintering process, the sintering temperatures were increased with cerium content. Detailed procedures for cathode preparation are presented elsewhere [17]. In this way, different samples were prepared containing 0.3, 0.5, 1.0, 1.5 and 5.0 wt.% of CeO_2 (Ni–Ce$_n$ cathodes). As the nickel cathodes are transformed to nickel oxide in an operating MCFC, because oxygen contacts the cathode at 650°C samples were oxidized before all these studies by treating them at 650°C air (NiO–Ce$_n$ cathodes). All the samples prepared were studied by XRD (SEIFERT 3000P diffractometer) and SEM (ISI DS-130) and their surface area and porosimetry were measured using a Micrometrics Pore Sizer 9310.

Corrosion behaviour of the samples produced was examined after immersion in a 62 Li_2CO_3/38 K_2CO_3 eutectic carbonate melt at 650°C under an oxidizing gas mixture of 80 CO_2/20 O_2. Samples of the eutectic were extracted after different exposure times and the nickel content determined by atomic absorption spectrometry using a Perkin-

Elmer 3030 spectrophotometer. Before measurements, a treatment to eliminate alkaline cations (Li^+ and K^+) from the eutectic was implemented in order to minimize interference.

3. Results and discussion

3.1. Cathode characterization

Table 1 shows textural characteristics of the cathodes prepared. Oxidation processes produce a decrease of the porosity in the nickel oxide samples, however, this decrease is lower if the sample contains cerium. Pores have a homogenous size with an average diameter consistent with the required values of ~ 7 μm. Cathodes with cerium (Fig. 1b and c) showed the same pore size distribution curve types as the reference Ni cathode (Fig. 1a).

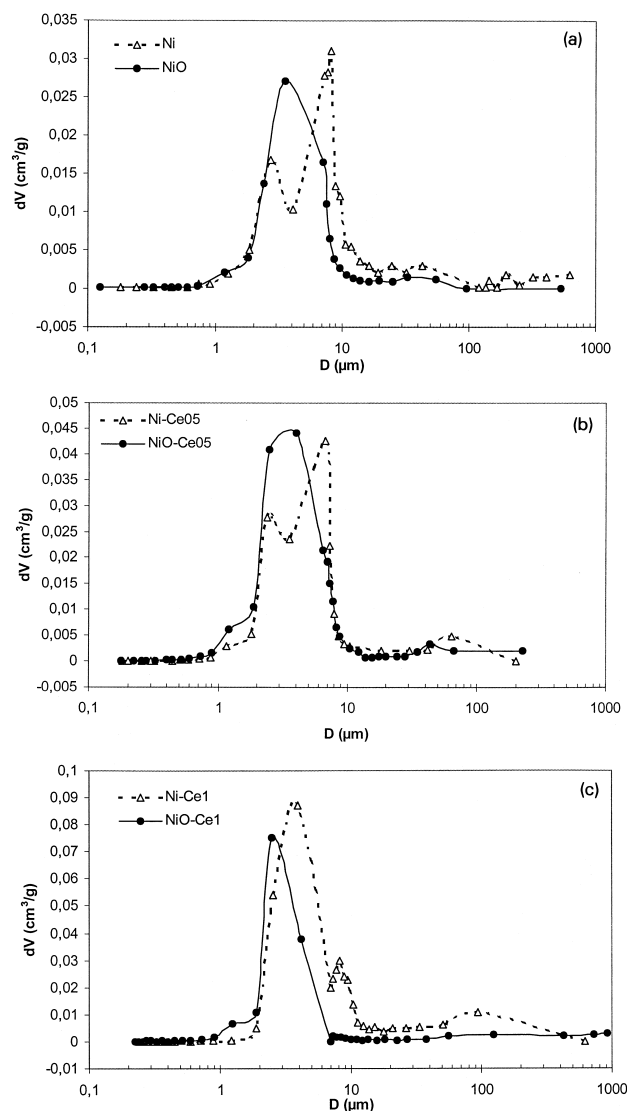Fig. 1. Pore distribution curves: (a) Ni and NiO cathodes; (b) Ni–Ce$_{05}$ and NiO–Ce$_{05}$; (c) Ni–Ce$_{10}$ and NiO–Ce$_{10}$.

The presence of cerium also has some effects on the nickel oxidation; this process is faster when cerium has been incorporated, as indicated by the XRD results. Peaks corresponding to CeO_2 were only visible in the diffractogram for concentrations higher than 1 wt.% CeO_2. No peaks corresponding to other cerium oxides or mixed Ce–Ni compounds were detected [18].

The sintering process was followed by SEM. From Fig. 2, it is evident that the cerium impregnated cathodes (Ni–Ce_n) have the same morphology as in the case of the Ni cathode.

3.2. The corrosion and the lithiation process

One of the most important problems presented by nickel cathodes is that the nickel extracted by corrosion of the cathodes causes cell deterioration. Therefore, the first test selected was to check if incorporation of cerium oxide would affect the corrosion process of nickel cathodes. From chemical analysis of the eutectic, nickel dissolution time, Vs, was determined for all cathodes prepared for total exposure times up to 200 h. Fig. 3 shows that minimum dissolution rates were evident for cathodes with 0.3–1 wt.% cerium oxide content. Initially, the cerium-free sample showed the highest dissolution rate, but after 20 h treatment, the rate was similar to that of the cerium
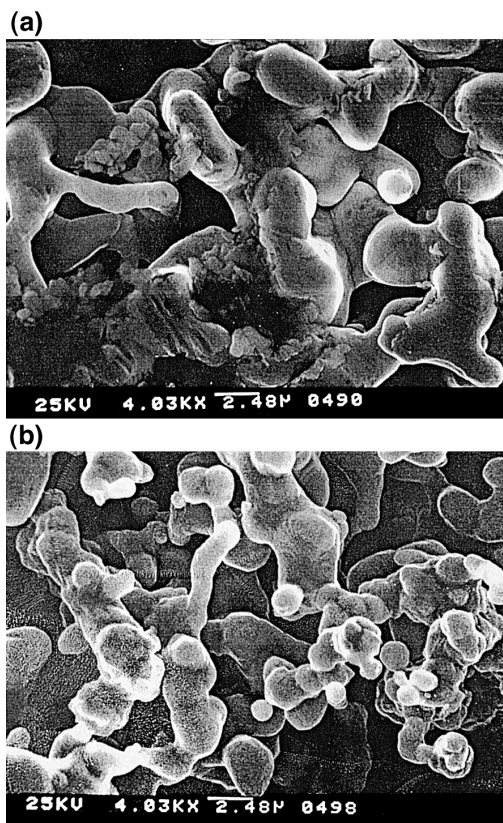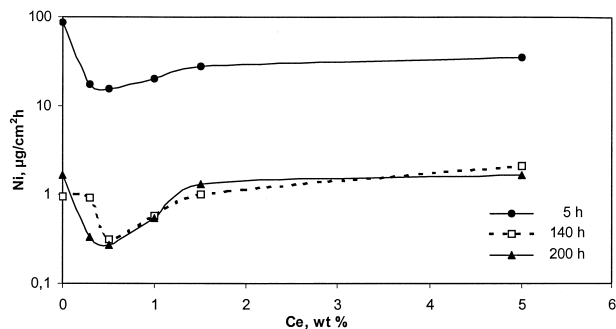

Fig. 3. Dissolution rate of nickel as a function of the CeO_2 content of NiO–Ce_n cathodes for several exposure times.

containing samples (Fig. 4). The dissolution rate of NiO cathodes and those containing less than 1% CeO_2 were similar for exposure to molten carbonates between 20 and 120 h. However, for longer corrosion times, the dissolution rate increased slightly for the cerium-free sample, while it decreased for the 0.3–1.0 wt.% of CeO_2. The values of the dissolution rate after 170 h increase with the cerium content for samples 1.5 and 5.0 wt.% CeO_2. These results clearly indicate that the corrosion process is affected by the incorporation of cerium in the sample and that, for low cerium concentrations, this effect is significantly positive for times longer than 100 h.

The original oxidized samples and those obtained after treatment in molten carbonate for different times were examined by SEM (Fig. 5); the composition of their surfaces was determined by microanalysis and XPS. From these results, it can be concluded that only the samples with high cerium content showed separated CeO_2 particles and that the nickel oxide surface layers showed a more compact structure in the case of the cerium containing samples. The corrosion treatment produce marked modifi-
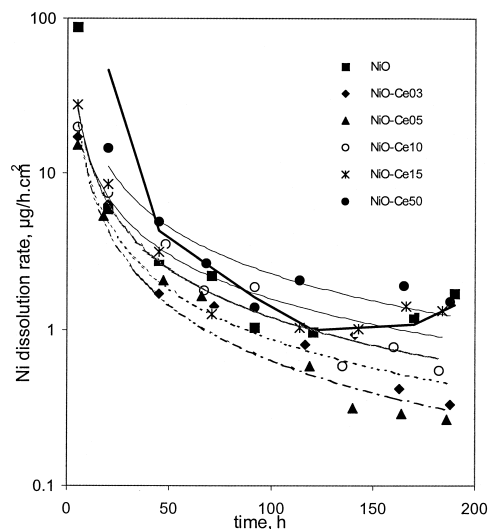

(a)

(b)

Fig. 2. Cathode morphology after sintering: (a) Ni; (b) Ni–Ce_{03}.

Fig. 4. Dissolution rate of nickel as a function of time for NiO–Ce_n cathodes.
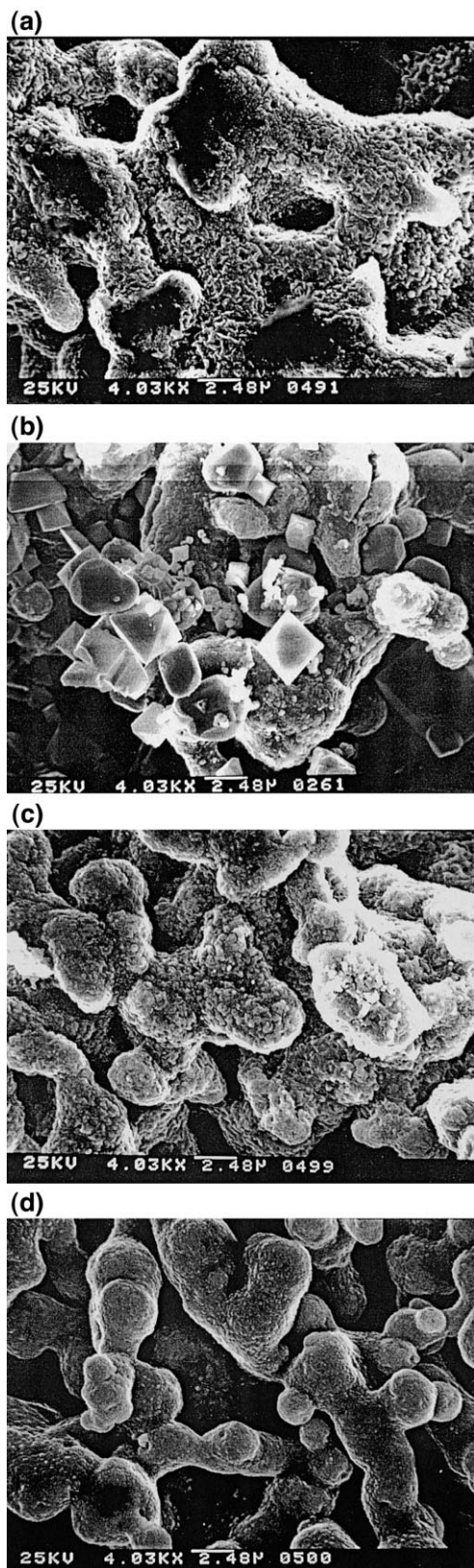
cations on the samples surfaces that appear more important for the cerium-free sample (Fig. 5b and d).

The variation of the nickel dissolution rate with time for NiO cathode indicates that the corrosion process is not taking place under constant conditions, rather the conditions at the sample surface are modified with the time of exposure to the carbonates. These surface modifications affect the nickel oxide corrosion process. Different authors have reported that nickel oxide incorporates lithium cations from the molten carbonates during fuel cell operation. This lithium incorporation introduces modifications in the surface composition and, probably, affects the corrosion process. In the case of the cerium containing samples, after an initial decrease, the dissolution rate reaches a relatively constant value that depends on the cerium content. These two different steps indicate that the corrosion process in these samples is also affected by lithiation. The differences between the curves corresponding to the cerium-free and the cerium containing samples (Fig. 4) indicate that the lithiation process is affected by the presence of cerium.

The effect of the presence of cerium on lithiation is indicated by the XRD data in Fig. 6. The displacement of the diffraction peaks at about $2\theta = 37°$ is considered to be due to the introduction of Li^+ ions into the NiO lattice. Consequently, Ni^{2+} ions are substituted by Ni^{3+}, thus decreasing the lattice parameter. It is noticed that cerium oxide favors the lithiation process, resulting in a mixed oxide with a higher Li^+ content that is a more conductive and stable cathode.
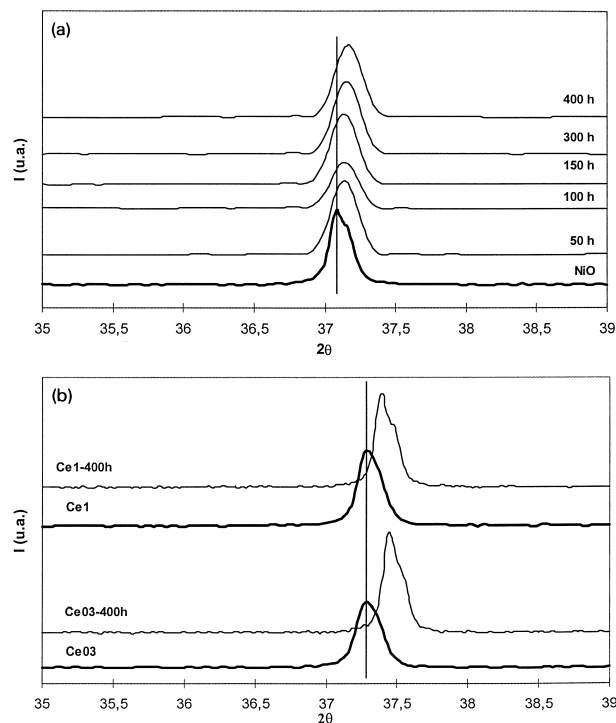

Fig. 5. SEM micrograph of the original oxidized cathodes and after test corrosion for 180 h: (a) NiO; (b) NiO post-test; (c) $NiO-Ce_{03}$; and (d) $NiO-Ce_{03}$ post-test.

Fig. 6. XRD patterns after test corrosion up to 400 h: (a) NiO; (b) $NiO-Ce_{03}$; and $NiO-Ce_{10}$.

4. Conclusions

The results of this study indicate that the incorporation of cerium into the nickel oxide surface modifies the composition and properties of this surface. For low cerium content, the corrosion process is retarded and the lithiation process is modified. Therefore, cerium incorporation can be used to introduce beneficial effects without damaging the desirable characteristics of nickel oxide as cathode for MCFC.

The results also show that the lithiation process is a very important factor that can improve the efficiency of the cell, but needs to be controlled because it can produce very damaging effects, such as the modification of the cathode volume by the formation on new compounds. Some of these problems can be solved by ex situ lithiation, but finding ways to control the lithiation process could open new ways to produce more efficient cathodes to be used on an industrial scale.

Acknowledgements

References

[1] L. Goirgi, M. Carewska, M. Patriarca, S. Scaccia, E. Simonetti, A. Di Bartolomeu, J. Power Sources 49 (1994) 227.
[2] T. Nishima, I. Uchida, J.R. Selman, J. Electrochem. Soc. 141 (1994) 1191.
[3] P. Tomczyk, G. Mordarsky, J. Electroanal. Chem. 304 (1991) 85.
[4] L. Giorgi, M. Carewska, S. Scaccia, E. Simonetti, E. Giaconetti, R. Tulli, Int. J. Hydrogen Energy 21 (1996) 491.
[5] W.H.A. Peelen, M. van Driel, K. Hemmes, J.H.W. de Wit, Electrochim. Acta 43 (1998) 3313.
[6] R.C. Makkus, K. Hemmes, J.H.W. de Wit, J. Electrochem. Soc. 141 (1994) 3429.
[7] E.S. Shedd, T.A. Henri, in: Proc. 3rd Rare Earth Res. Conf., April 1963, Clearwater, FL,1963, pp. 21–27.
[8] M.L. Orfield, D.A. Shores, J. Electrochem. Soc. 135 (1987) 1662.
[9] C.E. Baumgartner, J. Am. Ceram. Soc. 69 (1986) 162.
[10] K. Otta, S. Mitsusshima, S. Sato, S. Asano, H. Yoshitake, N. Kamiya, J. Electrochem. Soc. 139 (1992) 667.
[11] M.L. Orfield, D.A. Shores, J. Electrochem. Soc. 136 (1989) 2862.
[12] K. Hatoh, J. Niikura, E. Yasumoto, T. Gamo, J. Electrochem. Soc. 141 (1994) 1725.
[13] J. Pickering, P.J. Maddox, J.M. Thomas, Chem. Mater. 4 (1992) 994.
[14] C.E. Baumgartner, J. Electrochem. Soc. 131 (1984) 1850.
[15] I.J. Davidson, J.E. Greedan, U. von Sacken, C.A. Michal, W.R. Mickinson, J. Solid State Chem. 105 (1993) 410.
[16] T. Nishina, S. Ohuchi, K. Yamada, I. Uchida, J. Electroanal. Chem. 408 (1996) 181.
[17] L. Daza, CSIC Report, Spain, December 1993.
[18] J. Baranda, PhD Thesis, Universidad Autónoma de Madrid, Spain, 1997.