

Influence of lanthanum oxide as quality promoter on cathodes for MCFC

M.J. Escudero^a, X.R. Nóvoa^b, T. Rodrigo^c, L. Daza^{a,c,*}

^aDpto. Combustibles Fósiles, CIEMAT, Av. Complutense 22, 28040 Madrid, Spain

^bUniv. de Vigo, ETSEI, Lagoas-Marcosende 9, 36200 Vigo, Spain

^cInstituto de Catálisis y Petroleoquímica, CSIC, Campus Cantoblanco, 28049 Madrid, Spain

Abstract

A novel material based on lithium nickel mixed oxides modified by lanthanum impregnation was investigated as an alternative cathode for molten carbonate fuel cells (MCFCs). The electrochemical behaviour of the new cathode material was evaluated in an eutectic mixture of lithium and potassium (Li:K, 62:38) at 650 °C by electrochemical impedance spectroscopy (EIS) as a function of lanthanum content, immersion time and gas composition. The impedance spectra inform on electrode structural changes during the first 100 h. The loss of lithium and the low dissolution of nickel and lanthanum are responsible of these changes. Later on, the structure reaches a stable state. The lanthanum-impregnated cathodes show higher catalytic activity for oxygen reduction and lower dissolution of nickel oxide than the lanthanum-free sample. The cathode material having 0.3 wt.% of La₂O₃ shows the best behaviour. The loss of lithium was confirmed by X-ray diffraction (XRD) and inductive coupled plasma-atomic emission spectroscopy (ICP-AES). © 2002 Published by Elsevier Science B.V.

Keywords: Lithium nickel oxide; Molten carbonate; Fuel cell; Cathode; Lanthanum; EIS

1. Introduction

The molten carbonate fuel cell (MCFC) is believed to be one of the most promising new energy conversion devices that convert chemical energy in fossil fuels into electricity [1]. It is a highly efficient and environmentally clean source of power. Research and development on MCFCs have been performed in several countries and many researchers have made vigorous efforts to improve cell life and performance [2,3]. The current MCFC configuration is affected by two problems: the structural materials corrosion and the dissolution of the NiO cathode [4–6]. In order to improve the stability of NiO, alkaline earth metal salts have been added to the molten carbonate electrolyte, and new cathode materials have been developed [7–9]. To date, doped LiFeO₂, Li₂MnO₂ and LiCoO₂ have been considered as candidates for the cathode materials [10–14]. The electrical conductivity of these materials has been significantly improved by doping and may be considered acceptable. However, the porous cathode performance is usually lower than that of the reference NiO [15].

Hatoh et al. have shown that Li_xNi_{1-x}O with high-lithium content ($x > 0.2$) has a relatively lower rate of solubility

than the Li_xNi_{1-x}O cathode with lower lithium content ($0.02 < x < 0.05$) obtained with the in situ oxidised and lithiated NiO [16]. Other researchers have also proposed high-lithium content cathodes and studied the relationship between the lithium content and the porosity of the cathode. They have shown that the porosity increases up to the composition 23 at.% Li, beyond which the porosity was nearly constant [17]. In our previous work, the effect of addition of rare elements on the behaviour of NiO has been investigated. It was found that the incorporation of less than 1.0 wt.% of rare earth elements has a two-fold effect: decreases cathode dissolution rate and increases NiO cathode lithiation rate [18]. Thus, the incorporation of lanthanum ions appears to be a promising way of modifying the nickel oxide properties.

The lanthanum oxide has diverse industrial and technological applications. It is used as an important component in automobile exhaust-gas convectors, as catalyst support in the formation of ethanol, as a refractory oxide for calcium lights and optical glass in the formation as a core for carbon-arc electrode [19,20]. It is believed that the incorporation of lanthanum will act as an oxygen buffer and help nickel oxide lithiation. Peng et al. observed that the incorporation of La₂O₃ to NiO reduces grain size and could enhance cracking resistance of the nickel oxide [21].

A novel cathode material has been prepared by ex situ NiO lithiation to high-lithium content and lanthanum

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

impregnation, in order to decrease cathode dissolution rate and increase its catalytic activity for oxygen reduction. The present paper is aimed to study the effect of content lanthanum on the electrochemical behaviour of the new materials in molten carbonates. The study has been conducted using electrochemical impedance spectroscopy (EIS). The samples were analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and inductive coupled plasma-atomic emission spectroscopy (ICP-AES), before and after of exposure.

2. Experimental

2.1. Synthesis

Four different samples were synthesised using a solid-state reaction, one of them without lanthanum (named L_{40}), and the others containing 0.3, 0.5 and 0.8 wt.% of La_2O_3 (named $L_{40}La_{0.3}$, $L_{40}La_{0.5}$, and $L_{40}La_{0.8}$, respectively). Nickel powder (99.9% Johnson and Matthey) with a particle size between (3–7 μm), $La(NO_3)_3 \cdot 6H_2O$ (99.9% Johnson and Matthey) and Li_2CO_3 (99%, Panreac) were used as starting materials. Ni powder was added to a Li_2CO_3 solution prepared in distilled water to 0.4 lithium atomic fraction. For the samples containing lanthanum, $La(NO_3)_3 \cdot 6H_2O$ salt was dissolved in distilled water and added to the solution. A homogeneous mixture and partial water removal was obtained on rotating evaporator at 80 °C. Precursor samples were pressed into pellets at 20 Torr cm^{-2} for 5 min. The samples were calcined at 800 °C for 6 h.

2.2. Electrochemical measurements

The electrochemical characterisation of the new cathode materials was performed by means of EIS. The test cell was an alumina crucible contained in a covered stainless steel reactor. The cover of the reactor has been adapted to hold a thermocouple, a gas inlet/outlet and two electrodes. The cell was assembled with two nominally identical electrodes. Such a configuration allows elimination of the influence of the counter electrode and avoids the use of a reference electrode that is, by itself, a noise source [22]. Gold wires inserted in the core of each sample and shielded from the electrolyte by an alumina tube sealed by ceramic cement have made the electrical connections to the electrodes. Digital mass flow controllers/meters were used to provide the desired gas mixture composition of O_2 and CO_2 . The gas mixture was flowed into the melt through a long alumina tube.

The crucible was charged with 75 g of eutectic carbonate mixture (62 mol% Li_2CO_3 and 38 mol% K_2CO_3) and heated at 3 °C min^{-1} up to the operation temperature, 650 °C. Then, the electrodes were inserted in the carbonate melt and the cell temperature was kept at 650 °C.

The cell impedance was measured on immersion time with an exposure time of 200 h under an oxidising gas

mixture $CO_2:O_2$ of 40:10 to accelerate the dissolution of the cathode materials. The influence of gas composition was studied using atmospheres varying from 10 to 70% oxygen at 20% constant carbon dioxide (balance N_2), and from 10 to 80% carbon dioxide with 10% constant oxygen content (balance N_2).

The impedance spectra were recorded with an AUTOLAB system (PGSTAT30 and FRA2 module), from Eco Chemie B.V. The amplitude of the sinusoidal voltage signal for the impedance measurements was 5 mV. The measurements were performed at the open circuit potential, from 100 kHz down to 100 μHz at five points per frequency decade.

2.3. Structural characterisation and chemical analysis

The structure of the samples was characterised before and after the electrochemical tests by scanning electron microscopy (SEM) using a Hitachi S-2500 and XRD using a SEIFERT 3000 P diffractometer with a $Cu K\alpha$ radiation source. The Li, Ni and La contents of the samples were determined by ICP-AES (Jobin Yvon, JY-48/JY-38) before and after the electrochemical tests. The dissolution of nickel and lanthanum in the molten carbonate after the electrochemical tests were also analysed by ICP-AES.

3. Results and discussion

3.1. Electrochemical characterisation

Fig. 1 depicts the electrochemical impedance spectra for the four samples in an eutectic Li_2CO_3 – K_2CO_3 (Li:K, 62:38) at 650 °C under an oxidising gas mixture of $CO_2:O_2$ of 4:1 at different exposure time. As it can be seen from the corresponding Nyquist plots, two well-differentiated regions are present. In the high frequency region ($f > 1$ Hz), two arcs are present. The low frequency capacitive arc roughly increases on exposure time.

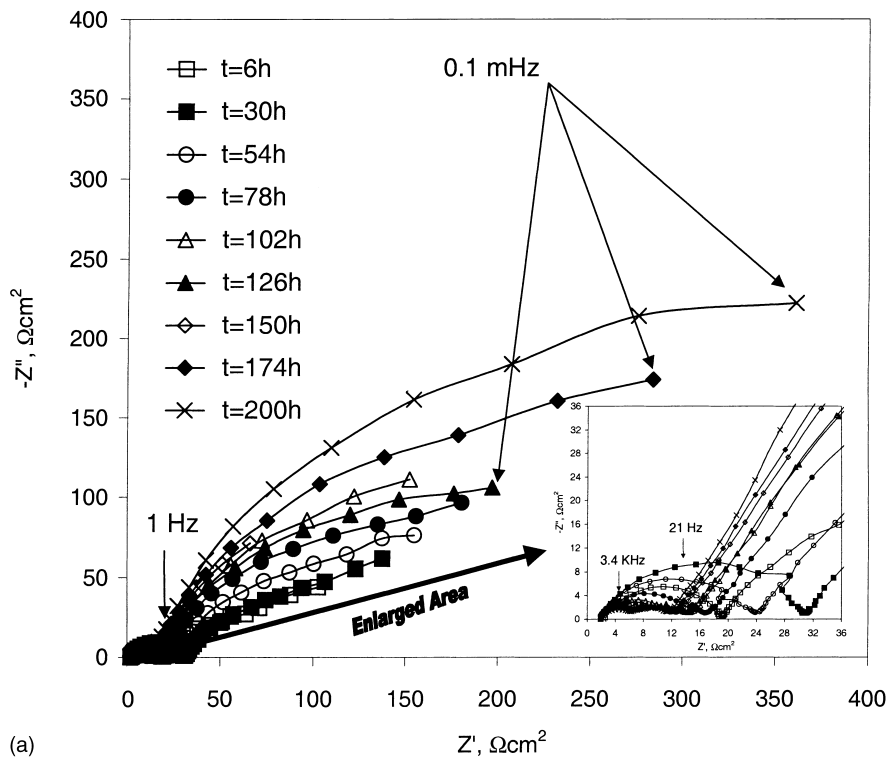
An interpretation for this impedance feature was given in our previous work based on lanthanum-free sample studies [23]. The proposed model is based in a transmission line that includes the particle-to-particle contact and the processes of charge-transfer, in addition to the impedance associated to the electric contact in the non-reactive material. The model allows assign a physical meaning to each one of the three time constants observed in the impedance spectra.

Between the two arcs present in the high frequency region, the one in the higher frequency range is associated to the intrinsic impedance of the non-reacting volume, and the one in the lower frequency range corresponds to the particle-to-particle contact impedance. This second arc shows important variations during the first 100 h of immersion, which can be attributed to the structural changes in the reactive surface of the electrode due to the dissolution of lithium and the oxidation of nickel. After that, the structure seems to reach a stable state.

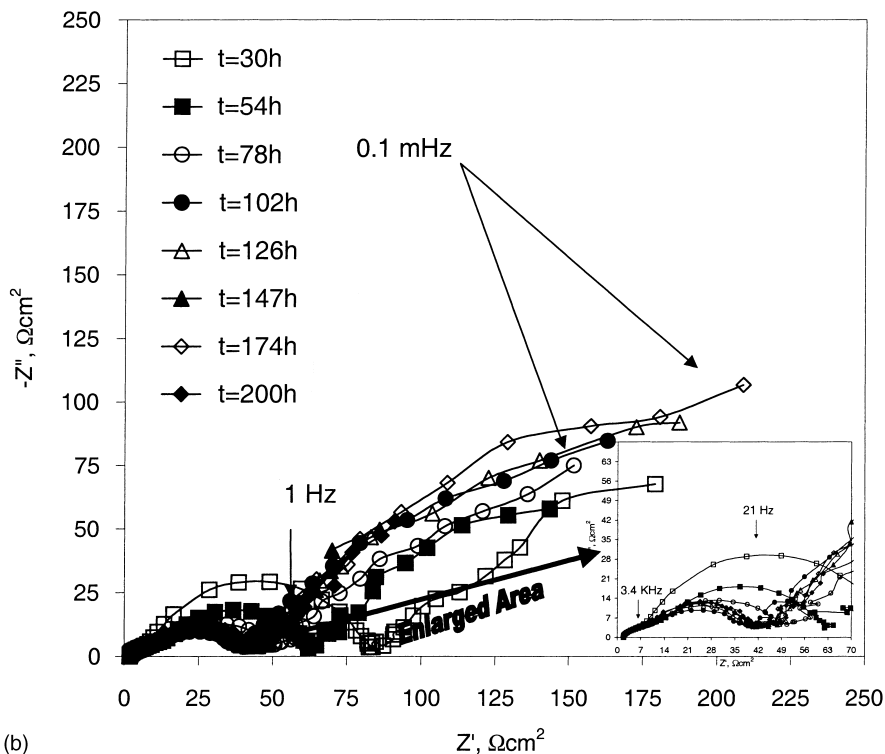
The third arc, in the low frequency region ($f < 1$ Hz), corresponds to the charge-transfer processes associated with the oxygen reduction and the oxide oxidation.

The dependence of the oxygen pressure at a constant p_{CO_2} of 0.2 atm for the sample with 0.8 wt.% of La_2O_3

is shown in Fig. 2. The low frequency arc decreases as p_{O_2} increases, while the arcs in the high frequency region are not influenced by O_2 content. This suggests that the process of oxygen reduction accelerates as p_{O_2} increases.



(a)



(b)

Fig. 1. Impedance spectra obtained for four samples as a function of immersion time: (a) L_{40} ; (b) $\text{L}_{40}\text{La}_{0.3}$; (c) $\text{L}_{40}\text{La}_{0.5}$; (d) $\text{L}_{40}\text{La}_{0.8}$.

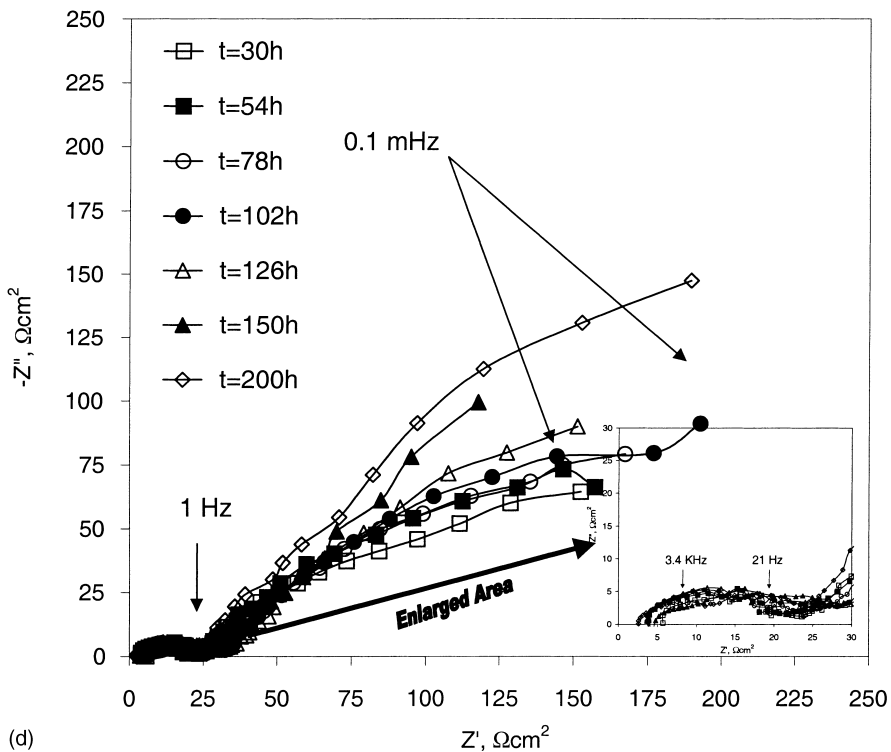
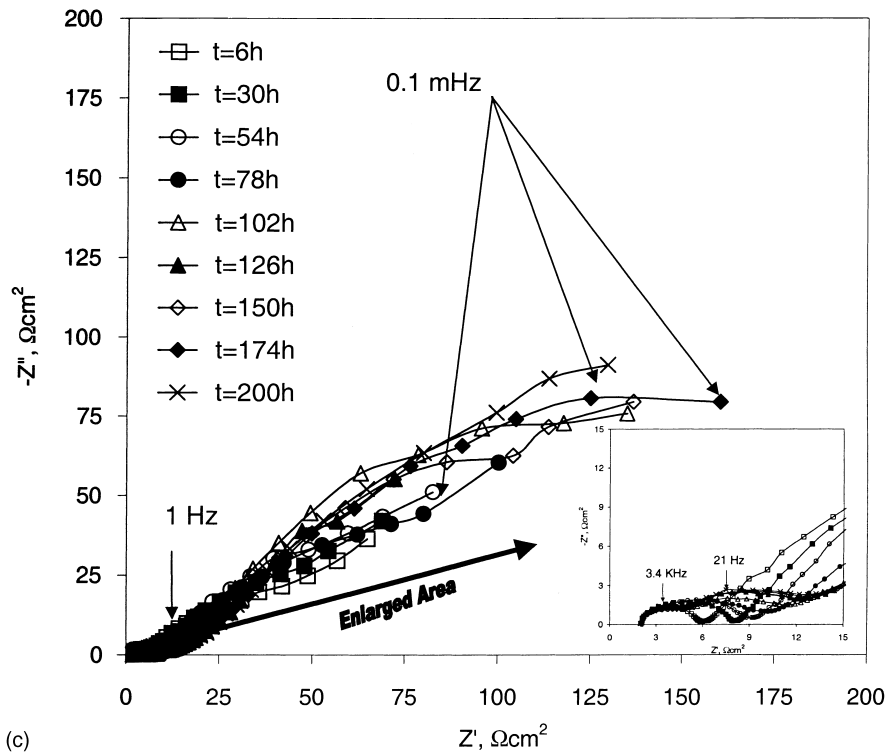


Fig. 1. (Continued).

Fig. 3 presents the impedance spectra as a function of carbon dioxide partial pressure at a constant p_{O_2} of 0.1 atm. The low frequency arc increases at higher p_{CO_2} . This indicate that the process of the charge-transfer is hindering by increasing p_{CO_2} . In the high region frequency, the second

arc at high frequency depends on the partial pressure of CO_2 that can be interpreted as an increasing difficulty of oxygen transport to the reactive surface increasing by lanthanum content. The influence of the gas composition for the lanthanum-free sample was discussed in our previous work

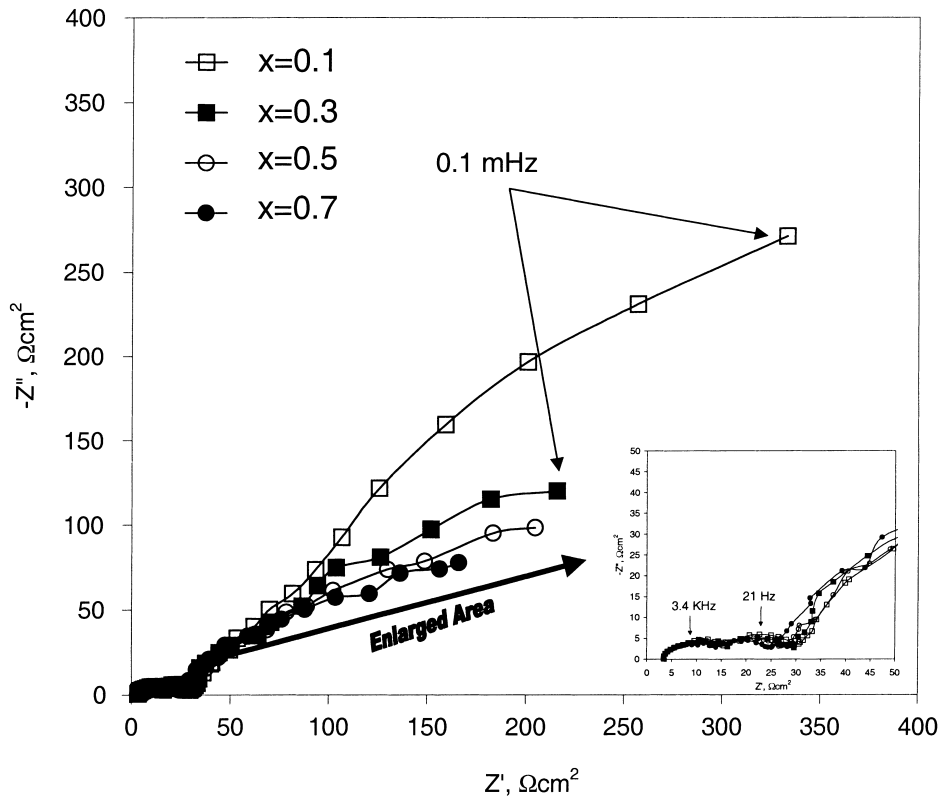


Fig. 2. Dependence of the impedance spectra obtained for $L_{40}La_{0.8}$ on oxygen content in the feeding gas at constant 20% CO_2 content (balance N_2); x denotes O_2 volume fraction.

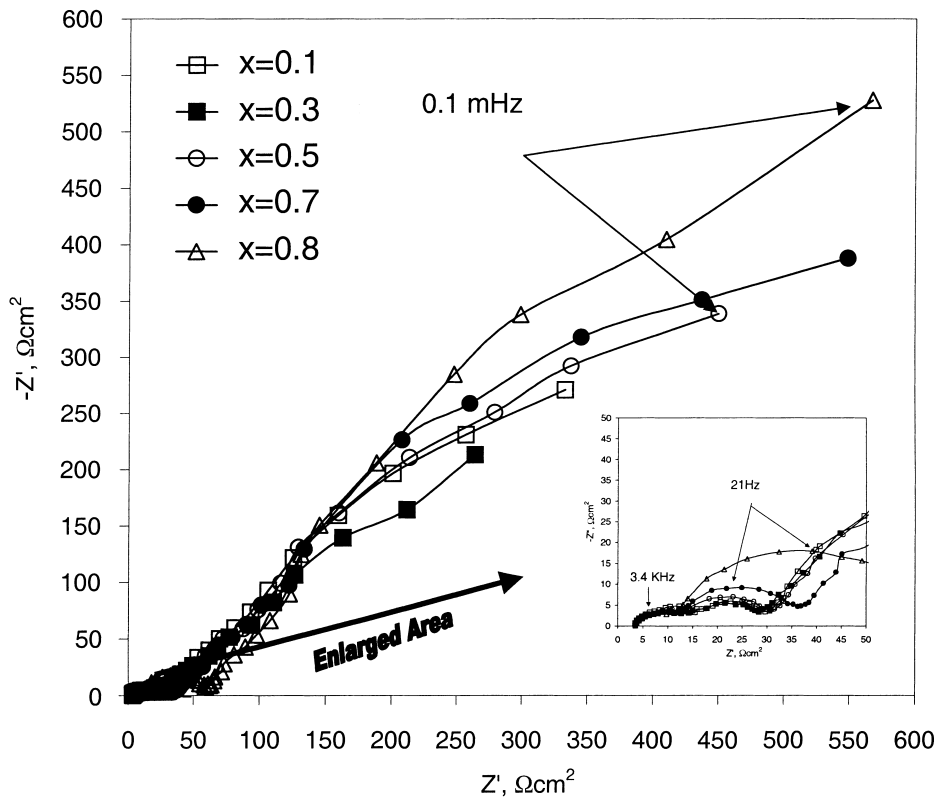


Fig. 3. Dependence of the impedance spectra obtained for $L_{40}La_{0.6}$ on CO_2 content in the feeding gas at constant 10% O_2 content (balance N_2); x denotes CO_2 volume fraction.

[23]. Similar results were obtained for the dependence of p_{CO_2} in the high frequency region where the shape of the spectra in the second arc is only sensitive at high p_{CO_2} .

The influence of the lanthanum content at 100 and 200 h of exposure in molten carbonate is depicted in Fig. 4. As can

be seen, the arc at low frequencies is smaller for the sample containing lanthanum. The samples having lower lanthanum content present lower capacitive arcs. That suggested that lanthanum has a positive influence in the charge-transfer processes associated with the oxygen reduction and the

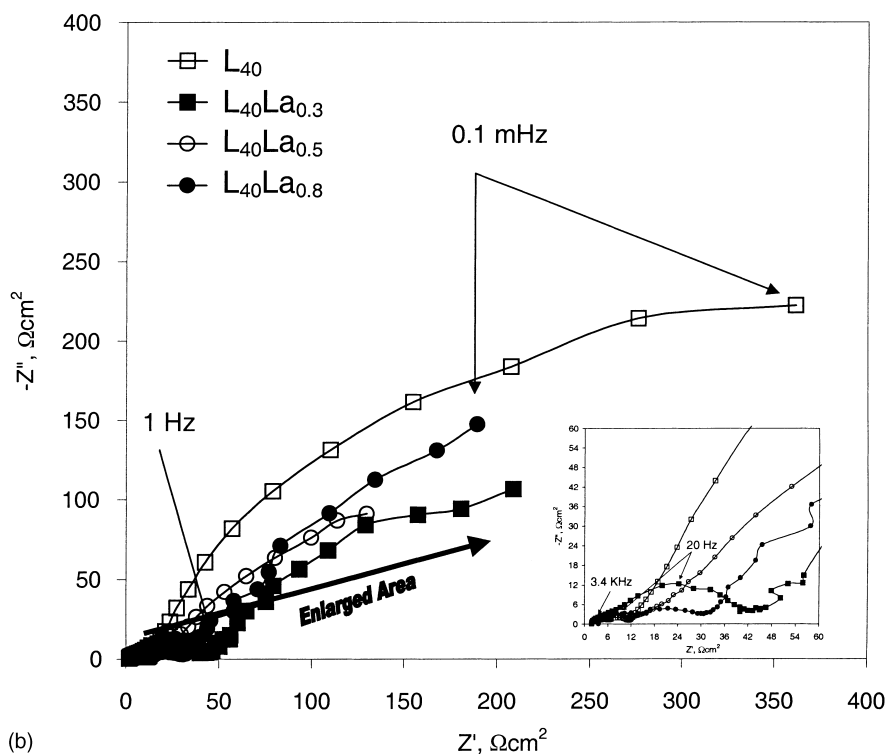
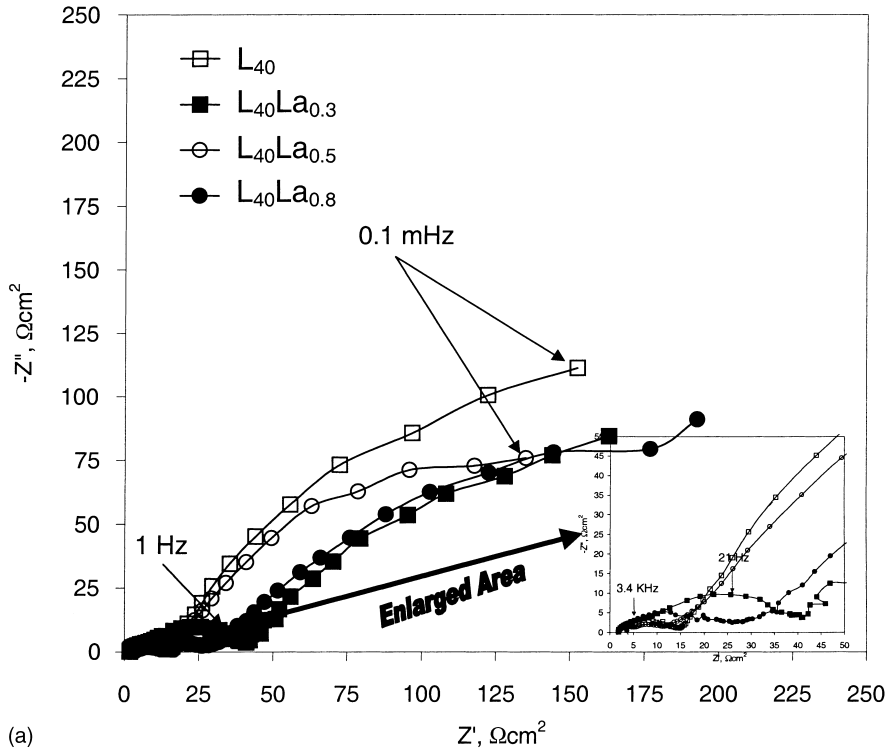


Fig. 4. Impedance spectra obtained at different immersion times: (a) 100 h; (b) 200 h.

oxide oxidation, being this effect more important at lower lanthanum concentration. In the high frequency region, the capacitive arcs do not present a clear dependence on lanthanum content. This can be understood if the effect of lanthanum in the contact impedance lies in the same order of magnitude than the experimental error.

3.2. SEM characterisation

Fig. 5 shows scanning electron micrographs of the four samples studied before and after the exposure in molten carbonate during 200 h under a gas mixture of $\text{CO}_2:\text{O}_2$ of

4:1. In general, similar morphology was observed for the four samples before the electrochemical test. After the electrochemical tests, the four samples showed slight morphological change that appears more important for the lanthanum-free sample.

3.3. XRD characterisation

The XRD patterns of the samples are depicted in Fig. 6. Initially, all samples showed the common presence of (0 0 3) and (1 0 4) peaks that reveals the formation of LiNiO_2 rhombohedral structure (Fig. 6a). Due to the low lanthanum

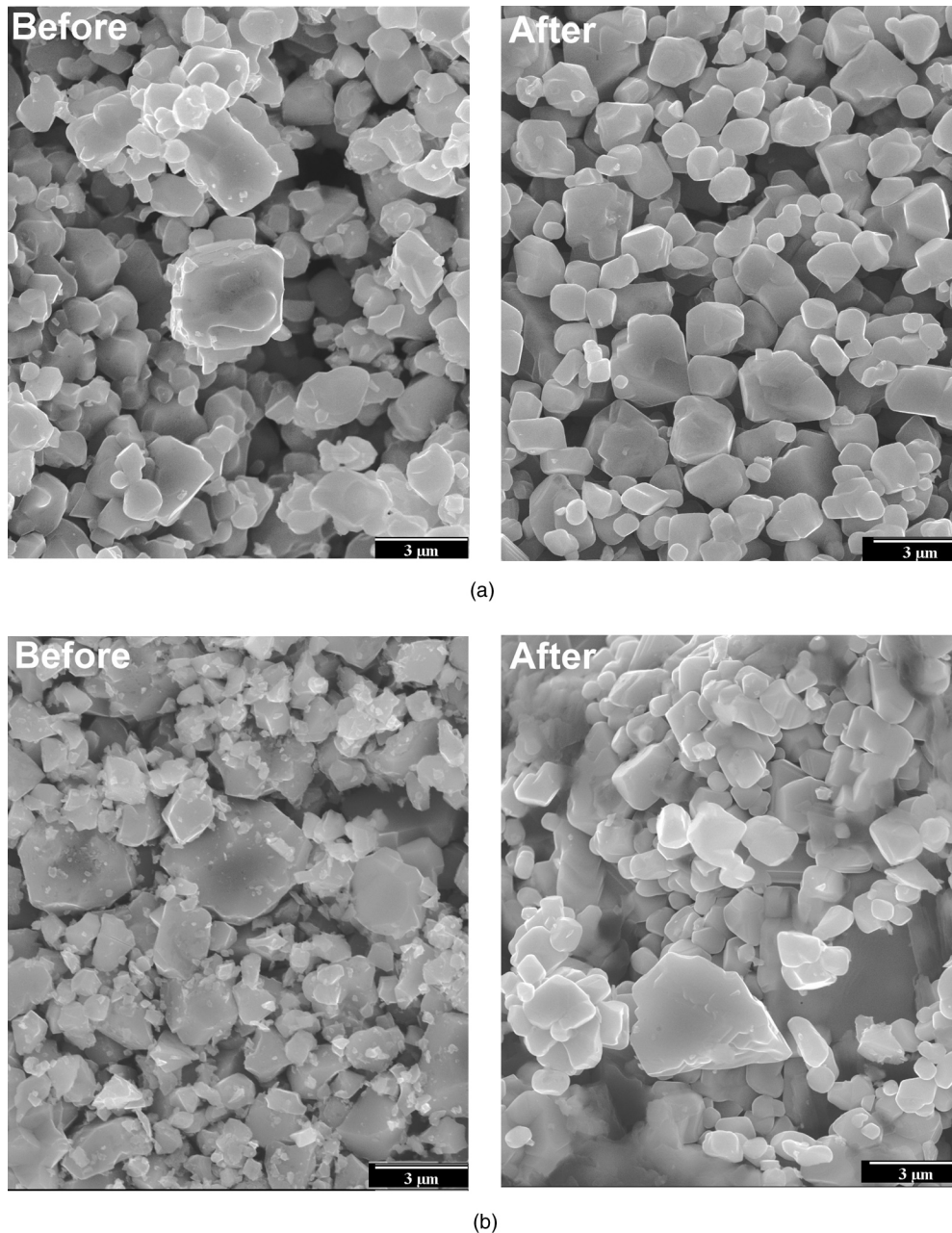


Fig. 5. SEM micrographs corresponding to the four samples before and after testing: (a) L_{40} ; (b) $\text{L}_{40}\text{La}_{0.3}$; (c) $\text{L}_{40}\text{La}_{0.5}$; (d) $\text{L}_{40}\text{La}_{0.8}$.

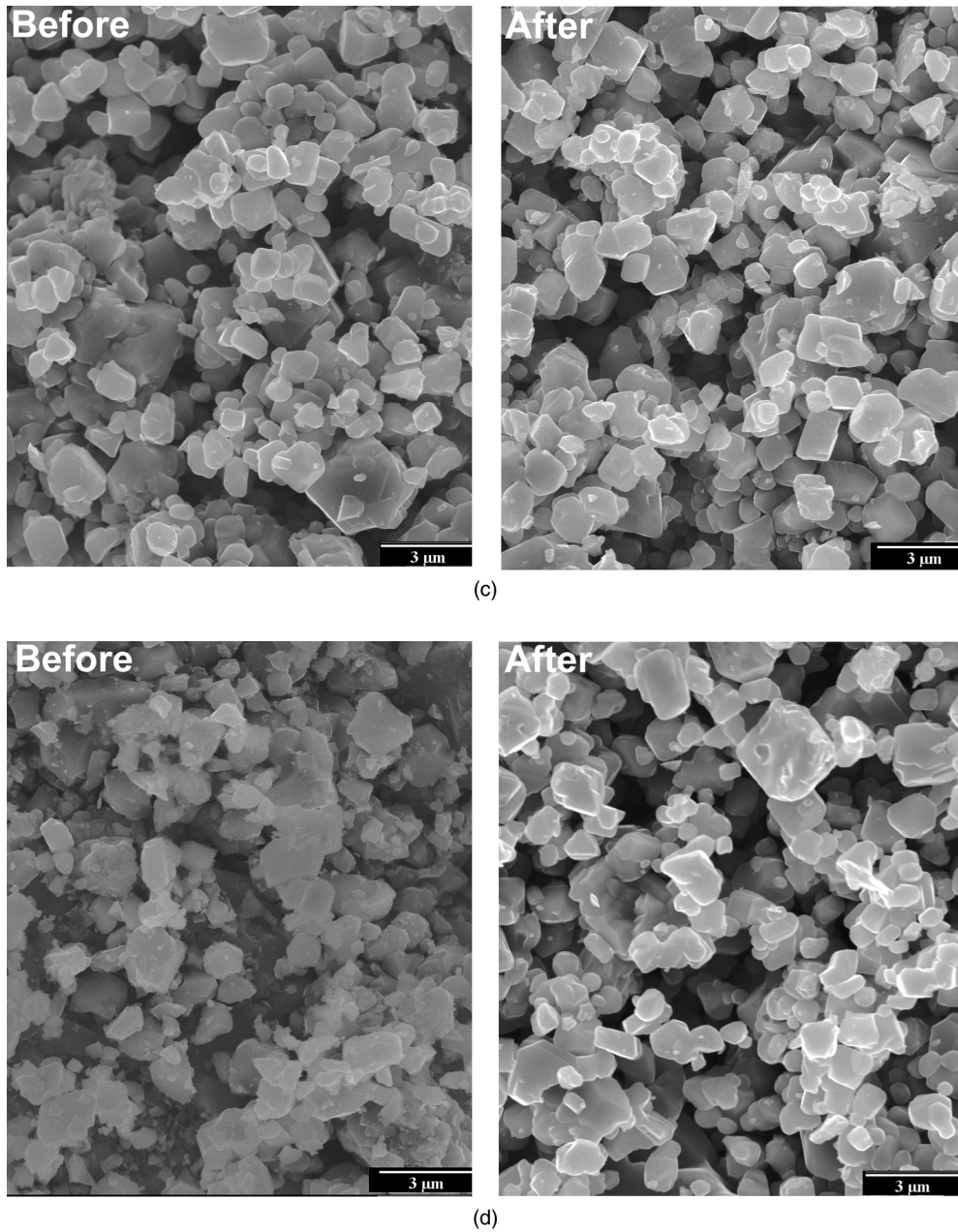


Fig. 5. (Continued).

content (<1%), the La_2O_3 structure cannot be detected. After the electrochemical test, the samples exhibited modifications maintaining the crystalline structure although a loss of lithium was observed (Fig. 6b). This is probably due to the diffusion of lithium ions from the electrode to the eutectic melt.

3.4. Chemical analysis

Chemical analysis showed that the samples suffer a loss of lithium and lanthanum (Table 1). The loss of lithium evaluated was between 17 and 30%. The sample with 0.3 wt.% of La_2O_3 presents higher lithium content than the other

samples. After the immersion, the lithium content in the samples was one order of magnitude higher than that estimated for in situ lithiated nickel oxide (1–4 at.%) formed in molten carbonate that is used as a cathode material in MCFC [24]. The loss of lanthanum was between 14 and 30% being lower for the sample with 0.8 wt.% La_2O_3 content.

The nickel concentrations measured in the carbonate after 200 h at 650 °C under a gas mixture of $\text{CO}_2:\text{O}_2$ of 40:10 was 12 ppm ($\mu\text{g Ni/g}$ electrolyte) for the lanthanum-free sample. For the samples with lanthanum, the amount of La in the eutectic was between 3 and 5 ppm, while the nickel content in the electrolyte decreased from 3 to 7 ppm due to the preferential dissolution of La_2O_3 .

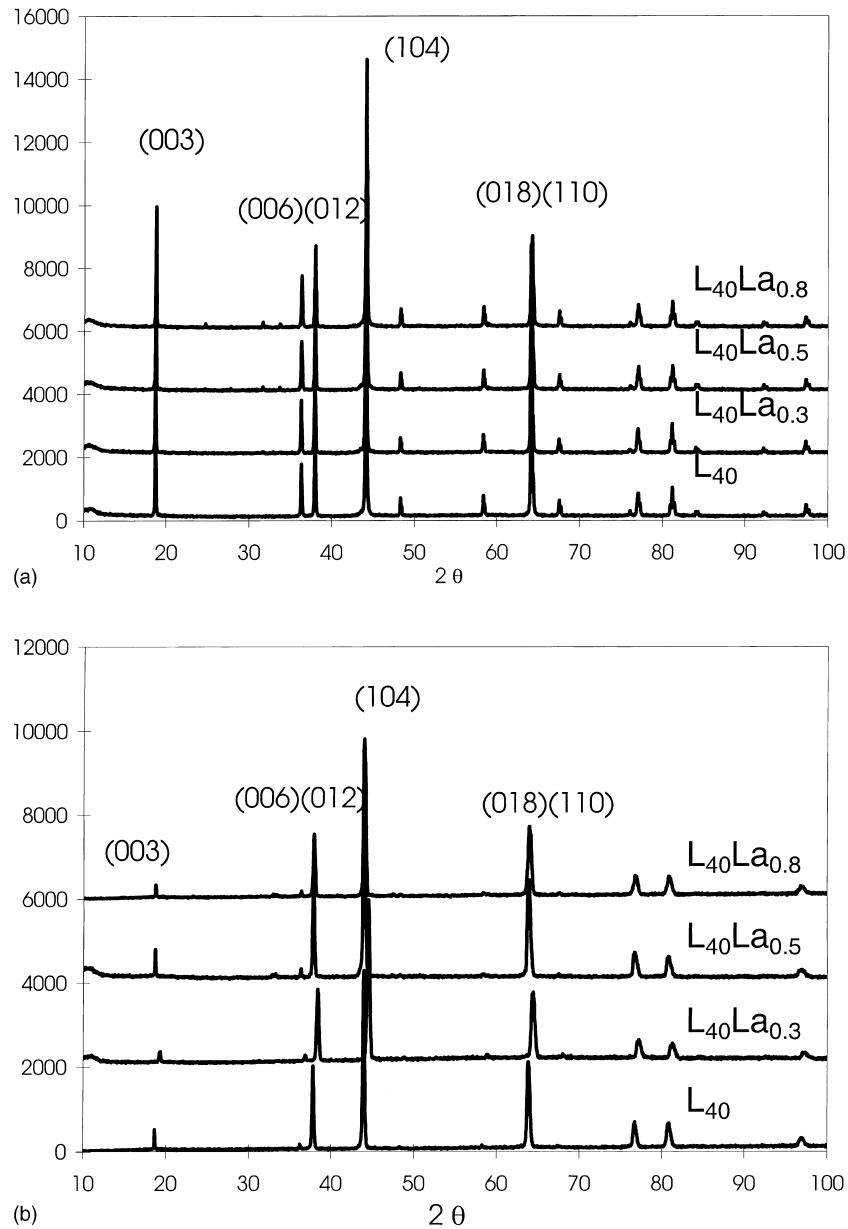


Fig. 6. XRD patterns for the four samples: (a) before testing; (b) after testing.

Table 1

Chemical analyses of the samples before and after the electrochemical tests and the nickel and lanthanum content in the eutectic

	Sample				Eutectic	
	wt.% Li (before)	wt.% Li (after)	wt.% La ₂ O ₃ (before)	wt.% La ₂ O ₃ (after)	Ni (ppm)	La (ppm)
L ₄₀	4.40	3.10			12	
L ₄₀ La _{0.3}	4.40	3.40	0.26	0.18	1.3	26
L ₄₀ La _{0.5}	4.40	3.00	0.50	0.42	6.6	33
L ₄₀ La _{0.8}	4.50	2.70	0.81	0.69	2.0	34

4. Conclusions

The behaviour of the ex situ NiO lithiated cathodes modified by impregnation with 0.3–0.8 wt.% of La₂O₃ in molten carbonate at 650 °C was investigated by EIS as a

function of immersion time and the partial pressure of O₂ and CO₂.

The impedance spectra show modifications during the first 100 h of immersion that are attributed to structural changes in the surface, mainly due to the lithium extraction

from the surface. The samples impregnated with lanthanum improved the charge-transfer processes associated with the oxygen reduction and mixed oxide oxidation, but it is better for low lanthanum content.

XRD and SEM confirmed the structural and morphology changes, respectively. Chemical analysis of the samples and eutectic showed a loss of lithium and lanthanum. However, the dissolution of nickel decreases in one order of magnitude for the sample impregnated with lanthanum.

It can be said that the sample with 0.3 wt.% of La_2O_3 shows the best behaviour because among the four tested samples (with and without lanthanum), this one presents the lower loss of lithium, the lower charge-transfer resistance and the lower nickel dissolution level.

These promising results indicate that the incorporation of low lanthanum concentrations into lithiated NiO could reduce nickel dissolution and improve the cell efficiency. Future research on the characterisation of the chosen material in single cell for >1000 h will be achieved to determinate if a promising candidate as cathode for MCFCs.

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