

# Porous nickel MCFC cathode coated by potentiostatically deposited cobalt oxide

## I. A structural and morphological study

M.J. Escudero<sup>a,\*</sup>, T. Rodrigo<sup>b</sup>, L. Mendoza<sup>c</sup>, M. Cassir<sup>c</sup>, L. Daza<sup>a,b</sup>

<sup>a</sup> Environment and Technology Research Centre (CIEMAT), Fossil Fuel department, Av. Complutense 22, 28040 Madrid, Spain

<sup>b</sup> Institute of Catalysis and Petrochemistry (CSIC), Campus Cantoblanco 28049, Spain

<sup>c</sup> Ecole Nationale Supérieure de Chimie de Paris (ENSCP), Laboratoire d'Electrochimie et de Chimie Analytique (UMR 7575 du CNRS), 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

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### Abstract

Porous nickel cathode was protected by potentiostatically deposited cobalt at different experimental conditions: oxidation potential and electrolysis duration. The deposition growth increased with the oxidation potential yielding a more developed granular structure with smaller grains. Thin layers of  $\text{Co}_3\text{O}_4$  were identified by X-ray diffraction (XRD) and Raman spectroscopy.  $\text{CoOOH}$  was detected by X-ray photoelectron spectroscopy (XPS) before annealing treatment and  $\text{Co}_3\text{O}_4$  after heating the sample at  $500^\circ\text{C}$  during 4 h in air. After this treatment, some morphological changes were observed on the coated samples due to grain compaction and oxidation of the nickel substrate. The porosity of the coated samples was relatively close to that of the sole porous nickel. These coatings exhibited an appropriate dual-pore structure with macro and micro pores, a basic MCFC requirement.

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### 1. Introduction

The interest of  $\text{LiCoO}_2$  as a candidate material for replacing the state-of-the-art molten carbonate fuel cell (MCFC) cathode,  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ , is well described in the literature [1–6]. This compound is less soluble than the nickel cathode in the MCFC conditions and has an electrocatalytical activity close to that of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ . However, its conductivity is lower than that of the usual cathode material, its mechanical resistance is lower and its cost is relatively high. In addition, problems in scale up of electrode area restrict its use. The thin layer technology is an interesting way of solving these practical problems by combining the properties of the  $\text{LiCoO}_2$  coating (low solubility) and the  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  substrate (cheap, good conduc-

tivity and mechanical strength). The feasibility of coating the nickel cathode with well-controlled  $\text{LiCoO}_2$  thin layers has been analysed in recent papers [7–10].

In a previous work, we have developed and optimised the electrochemical deposition of  $\text{Co}_3\text{O}_4$  thin layers on dense nickel or nickel oxide substrates [11,12]. This cheap and room-temperature technique allowed us to obtain thin and homogeneous layers of  $\text{Co}_3\text{O}_4$  transformed into  $\text{LiCoO}_2$  after exposure to the molten carbonate melt. The use of dense nickel or nickel oxide substrates was a first necessary step to analyse thoroughly the structural and morphological features of the cobalt coatings; nevertheless, the situation can be significantly different in the case of porous electrodes. The present paper is dedicated to the elaboration and characterisation of cobalt oxide deposits on the porous nickel cathode before its oxidation and lithiation in situ in molten  $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3$ , one of the

\* Corresponding author. Tel.: +34 91 3466 622; fax: +34 91 3466 269.  
E-mail address: [m.escudero@ciemat.es](mailto:m.escudero@ciemat.es) (M.J. Escudero).

Table 1  
Name and description of all the samples analyzed in the present study

Sample	E/V vs. Hg/Hg <sub>2</sub> Cl <sub>2</sub>	Electrolysis time (h)	Annealing treatment
Ni			No
NiCo0.50t8	0.50	8	No
NiCo0.65t8	0.65	8	No
NiCo0.50t24	0.50	24	No
NiCo0.65t24	0.65	24	No
NiO			Yes
NiOC0.50t8	0.50	8	Yes
NiOC0.65t8	0.65	8	Yes
NiOC0.50t24	0.50	24	Yes
NiOC0.65t24	0.65	24	Yes

candidate electrolytes for MCFC application, in the standard conditions. The structural properties of the deposits were characterised either directly or after an annealing treatment by X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS). The morphological features were analysed by scanning electron microscopy (SEM) associated with energy-dispersive spectroscopy (EDS) and the pore size deposition by mercury porosimetry.

## 2. Experimental

### 2.1. Electrochemical deposition

The samples were prepared by potentiostatic deposition of cobalt oxide films on porous Ni foils (6 mm × 25 mm × 0.5 mm). The deposition was performed in a four-compartment Tacussel glass cell with a 0.1 mol l<sup>-1</sup> Co(II) solution prepared from Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Fluka, with a purity of 99.99% analytical-reagent grade chemical) in a 0.5 mol l<sup>-1</sup> solution of NaNO<sub>3</sub> (Merck) with a pH = 4. The solution was de-aerated during 30 min prior to electrochemical deposition and the pH fixed at 7.4 by addition of a 1 mol l<sup>-1</sup> NaOH solution. The working electrode was a porous nickel foil, the counter electrode was a Pt foil and the reference electrode was a Hg|Hg<sub>2</sub>Cl<sub>2</sub> (SCE) which was placed in a separate compartment filled with a 0.5 mol l<sup>-1</sup> NaNO<sub>3</sub>. The potentiostatic deposition was performed by means of a Princeton Applied Research (PAR) Model 263 system. The effect of two different potentials 0.50 and 0.65 V versus SCE, at two different electrolysis durations 8 and 24 h, before and after thermal treatment (at 500 °C during 4 h in air at a heating rate of 1 °C min<sup>-1</sup>), on the cobalt oxide deposits, was investigated. All the samples studied in this work are reported in Table 1.

### 2.2. Characterisation techniques

XRD analyses were performed with a Philips Model X'Pert-MPD diffractometer using a Cu K $\alpha$  radiation ( $\lambda$  = 1.542 Å). The diffraction intensity was measured in the 2°–90° (2 $\theta$ ) range, by steps of 0.05° (2 $\theta$ ) with a counting time of 2 s.

Raman spectra were obtained at room temperature with a Bruker RFS-100 FT-Raman spectrometer provided with a diode-pumped germanium solid-state detector, which operates at liquid N<sub>2</sub> temperature. An Nd:YAG laser was used as exciting source. The samples were pressed into the holder with no other pre-treatment. A laser power of ca. 600 mW was used, the spectra being taken with a resolution 4 cm<sup>-1</sup> and accumulating 500 scans. For each measurement the integration time was 30 min.

XPS analysis was performed with a Perkin-Elmer PHI 5400 spectrometer equipped with a Mg K $\alpha$  excitation source ( $h\nu$  = 1253.60 eV) and a beam size of 1 mm diameter. Typical operation conditions were: X-ray gun, 15 kV, 20 mA, pressure in the sample chamber  $\sim 10^{-9}$  Torr, pass energy, 89.50 eV for general spectra (0–1100 eV) and 35.75 eV for high resolution spectra. In order to take into account the charging effects on the measured binding energies, these energies were determined by referencing to the C 1s peak at 284.8 eV.

The morphology and composition of the deposits were examined with SEM using a Hitachi microscope S-2500 combined with EDS, model Sun Sparcstation.

The porosity and the pore size distribution were determined by mercury porosimetry using a Micrometrics Pore Sizer 9310.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the cobalt oxide formed on the porous nickel foil obtained at 0.65 V during 24 h, before and after the thermal treatment (4 h at 500 °C in air). Initially, only the XRD peaks corresponding to metallic nickel were observed at 44.50°, 51.84°, and 76.37° (2 $\theta$ ). After the annealing treatment, apart of the XRD peaks of Ni, less intense peaks were detected: they correspond to NiO at 37.28°, 42.23°, and 62.97° (2 $\theta$ ) and to cubic Co<sub>3</sub>O<sub>4</sub> compound that appear at 19.00°, 31.27°, 36.85°, 59.35°, and 65.23° (2 $\theta$ ). This indicates that the formation of cubic Co<sub>3</sub>O<sub>4</sub> on porous Ni is only obtained after an annealing process. A similar behaviour was obtained for all the other samples, but the intensity of the peaks relative cubic Co<sub>3</sub>O<sub>4</sub> decreases with reducing both potential and electrolysis duration. However, it is difficult to obtain a detailed information about the crystallographic structure of deposits because the cobalt content is much lower than that of nickel.

Raman spectroscopy is a tool providing information on the vibrations of atoms in crystals and is very sensitive to the symmetry of crystallographic structures. The Raman spectra of the samples with cobalt deposits on porous nickel, before and after annealing treatment, are presented in Fig. 2. Initially, these samples showed two broad bands around 501 and 613 cm<sup>-1</sup> that did not appear in the porous nickel Raman spectrum. This suggests that these bands are due to the presence of cobalt on the porous substrate. The intensity of these bands increased with the imposed potential and the electrolysis duration and, therefore, with the cobalt content,

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