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Review

Porous nickel MCFC cathode coated by potentiostatically deposited cobalt oxide III. Electrochemical behaviour in molten carbonate

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Abstract

A cobalt oxide coating was deposited on porous nickel by a potentiostatic electrochemical technique and studied in molten $(Li_{0.52}Na_{0.48})_2CO_3$ eutectics at 650 °C under an atmosphere of CO_2:Air (30:70). The structural and morphological characteristics of this coating before and after immersion in the molten electrolyte were described in a previous paper, showing that the initial Co_3O_4 layer is rapidly transformed into $LiCoO_2$ and afterwards probably into $LiCo_{1-y}Ni_yO_2$. In the present part, the electrical and electrochemical behaviour of this promising novel MCFC cathode material was thoroughly analysed during 50 h by impedance spectroscopy. A porous nickel cathode was tested in the same conditions and taken as a reference. The oxidation and lithiation reactions are accelerated by the presence of cobalt. The charge transfer resistance is higher with the coated cathode but the diffusion resistance through this new material is lower in comparison with the state-of-the-art cathode.

Keywords: Electrochemical impedance spectroscopy; Nickel oxide; Cobalt oxide; Coating; Cathode; Molten carbonate fuel cell

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Contents

1. Introduction

In a previous study [1], we have investigated the behaviour of an MCFC Ni cathode, covered by electrochemically deposited cobalt oxide, in molten carbonates at 650 °C during 50 h under CO_2:Air (30:70) by XRD, Raman spectroscopy, XPS, SEM-EDS and mercury porosimetry. XRD revealed the presence of Co_3O_4 in the prepared cathode and a loss of cobalt after its immersion. Raman studies confirmed the initial presence of the Co_3O_4 spinel structure and its rapid transformation into $LiCoO_2$ and lithium–cobalt–nickel oxide ($LiCo_{1-y}Ni_yO_2$) in the molten eutectic. After exposure to the molten carbonate melt, the presence of Ni^{3+} was detected by XPS for the Co_3O_4-coated porous nickel, which is probably due to the lithiation of the NiO–Co sample. SEM micrographs revealed that the coated porous Ni

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suffered morphologic changes during the exposure in comparison with porous Ni. This was explained by the formation of $LiCo_{1-y}Ni_yO_2$ on the surface of porous nickel. Chemical analysis confirmed the dissolution of cobalt but an important reduction in the solubility of nickel in the case of the prepared cathode. The cobalt oxide on porous nickel sample presented after its immersion similar porosity and higher pore size than the porous nickel. These results showed that this coated material presents good features in order to be used as an alternative MCFC cathode.

In the present study, the electrical characteristics of the coated material were thoroughly analysed by impedance spectroscopy in molten $(Li_{0.52}Na_{0.48})_2CO_3$ eutectics at 650 °C under a standard cathodic atmosphere of CO_2:Air (30:70). A pure porous nickel cathode was tested in the same conditions and taken as reference. This kind of analysis is of great interest in order to determine the conductivity of this cathode and to understand all the phenomena (mass and charge transfer, morphological changes, etc.) related to the electrochemical processes: these properties are essential for the selection of a good cathode material. Among the interesting studies using EIS to apprehend these phenomena, two interesting works should be mentioned. Yang and Kim [2] studied the oxidation behaviour of Ni–Co alloy deposited on a gold electrode and exposed to Li–K carbonate eutectic. They analysed the varied mechanistic processes (oxidation, diffusion, oxide growth, lithiation and oxygen reduction) by correlating OCP measurements to cyclic voltammetry and to experimental and simulated impedance data. Later, Ryu et al. [3] measured R_{ct}, R_{diff}, C_{dl} and CPE and showed their role in the understanding of the *in situ* reaction of the Ni–Co electrode, as well as the improvement of the electrocatalytic activity of Ni–Co with respect to the porous Ni cathode.

2. Experimental

2.1. Electrochemical deposition

The sample was prepared by potentiostatic deposition of cobalt oxide film on porous nickel sample according to a procedure fully described in previous papers [4,5]. The potentiostatic deposition was performed with a Princeton Applied Research (PAR) Model 263 system at 0.65 V versus SCE and an electrolysis times of 24 h. Then, the sample was annealed at 500 °C for 4 h in air at a heating rate of 1 °C min^{-1}.

2.2. Electrochemical characterisation

The electrochemical characterisation of the new cathode material was performed by means of EIS. The experimental cell used was described in previous work [6,7]. 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 [8]. The samples with a surface of 1 cm^2 were immersed into 75 g of lithium and sodium molten carbonates mixed in proportions of 52–48 mol% at 650 °C under a standard cathodic atmosphere of CO_2:O_2:N_2 (30:15:55). The cell impedance was measured as a function of immersion time during 50 h. A pure porous nickel cathode was tested in the same conditions and taken as reference.

The impedance spectra were recorded with an AUTOLAB with PGSTAT30 and FRA2 module (Eco Chemie B.V.). The amplitude of the sinusoidal voltage signal for the impedance measurements was 5 mV. The measurements were performed using five points per frequency decade between 100 kHz and 100 mHz at the open circuit potential. The impedance data were analysed by using the software Zview developed by J.R. McDonald.

3. Results and discussion

3.1. Previous remarks

In order to establish a sound interpretation of the impedance behaviour of Co_3O_4-coated Ni cathode, it is worthy to remind what are the important steps occurring when dipping an MCFC cathode in the molten carbonate eutectic, before reaching a stable potential due to the oxygen reduction, which can be written in a simplified mode, without taking into account ${O_2}^{2-}$ or ${O_2}^{-}$ species [9], as

$$0.5O_2 + CO_2 + 2e^- \rightarrow {CO_3}^{2-}$$

In the case of the nickel cathode, different steps are known to occur.

Under the cathode gaseous environment, the first step is due to nickel oxidation [10]:

$$Ni + CO_2 \rightarrow NiO + CO$$

The second step is due to the growth of the nickel oxide layer and to the increase in the resistance. Afterwards comes the third step which is the most important one for MCFC use, the influence of the alkali cations of the carbonate melt and, in particular, the lithiation phenomenon [10,11]:

$$(1-x)NiO + 0.5Li_2CO_3 + 0.25O_2 \rightarrow Li_x{Ni_x}^{3+}{Ni_{(1-2x)}}^{2+}O + 0.5CO_2$$

The value of x (0.002) has been determined in a previous study [12], deducing that the lithiated compound can be represented by $Li_{0.002}{Ni_{0.002}}^{3+}{Ni_{0.996}}^{2+}O$.

The phenomenon is even more complex because, on the one hand, a slight incorporation of Na^+ is possible in the mentioned eutectic and, on the other hand, NiO can be partially dissolved in the melt [13,14]:

$$NiO + CO_2 \rightarrow Ni^{2+} + {CO_3}^{2-}$$

In the case of the Co_3O_4 nickel cathode, apart of the specific reaction concerning the nickel species, cobalt oxide is spontaneously transformed into $LiCoO_2$. This compound can also be slightly dissolved in the carbonate melt:

$$LiCoO_2 + 1.5CO_2 \rightarrow Li^+ + Co^{2+} + 1.5{CO_3}^{2-} + 0.25O_2$$

Furthermore, knowing the possible existence of the mixed $LiCo_{1-y}Ni_yO_2$ species, the phenomena involved can be rather complex.