



Performance analysis of new cathode materials for molten carbonate fuel cells

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ABSTRACT

The slow dissolution of the lithiated nickel oxide cathode represents one of the main causes of performance degradation in molten carbonate fuel cells (MCFC). Two main approaches were studied in ENEA laboratories to overcome this problem: protecting the nickel cathode covering it by a thin layer of a material with a low solubility in molten carbonate and stabilizing the nickel cathode doping it with iron and magnesium.

Among several materials, due to its low solubility and good conductivity, lithium cobaltite was chosen to cover the nickel cathode and slow down its dissolution. A nickel electrode covered with a thin layer of lithium cobaltite doped with magnesium, was fabricated by complex sol–gel process. To simplify electrode preparation, no thermal treatments were made after covering to produce lithium cobaltite, and during the cell start-up $\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$ was obtained *in situ*.

To stabilize the nickel cathode, metal oxides Fe_2O_3 and MgO were chosen as dopant additives to be mixed with NiO powder in a tape-casting process ($\text{Mg}_{0.05}\text{Fe}_{0.01}\text{Ni}_{0.94}\text{O}$).

On the prepared materials TGA analysis, morphological analysis by scanning electron microscopy (SEM–EDS) and electrical conductivity measurements were carried out.

A conventional nickel cathode, the nickel cathode covered by lithium cobaltite precursors and the nickel cathode stabilized by iron and magnesium oxides were each tested in a 100 cm^2 fuel cell.

Polarization curves and internal resistance (iR) measurements were acquired during the cell lifetime (1000 h) and the effect of gas composition variation on the cell performance was studied.

From a comparison with the conventional nickel cathode it can be observed that the new materials have similar performance and show a good potential stability during the cell operating time. From the post-test analysis both the nickel cathode covered by lithium cobaltite and the nickel cathode doped with iron and magnesium seem to succeed in reducing nickel dissolution.

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1. Introduction

Molten carbonate fuel cells (MCFC) are in the class of high-temperature fuel cells. Developed in the mid 1960s, improvements have been made in fabrication methods, performance and endurance.

The higher operating temperature allows to use natural gas [1] without an external fuel processor or without previous fuel treatments, because methane reforming can take place directly inside the cell (with a catalyst), or utilising an integrated reformer element. The heat released from the hydrogen electrochemical oxidation provides energy for the endothermic reforming reaction, thus creating a closed energy balance.

Alternative energy sources, as low-Btu fuel gas from industrial processes, are generally characterised by a large fraction of fixed carbon and a conspicuous amount of contaminants, so that high-

temperature fuel cells are the most appropriate, being more tolerant to these compounds than fuel cells operating at low temperature.

MCFC uses a molten carbonate salts mixture as its electrolyte. The electrolyte composition varies, but usually consists of lithium and potassium carbonate which, at the operative temperature (650°), are liquid and suspended in a porous, insulating and chemically inert ceramic matrix ($\gamma\text{-LiAlO}_2$). At 650°C noble metal catalysts are not required for the electrochemical reactions: the anode is highly porous sintered nickel (Ni), alloyed with chromium to prevent creep problems, the cathode is a porous nickel oxide (NiO) material doped with lithium.

One of the main disadvantages of the MCFC is cathode dissolution that causes a serious problem by limiting cell life-time. Although a Ni cathode is preferred to other materials for its good conductivity and low cost, the lifetime of NiO in MCFCs is limited by its high solubility in molten carbonate that causes the dissolution and subsequent precipitation of Ni:Ni^{2+} cations diffuse along the tile to the anode side where they are reduced in presence of hydrogen to metallic nickel (Ni^0). The deposition of metallic Ni grains, creates short circuits thereby causing a rapid decay in the

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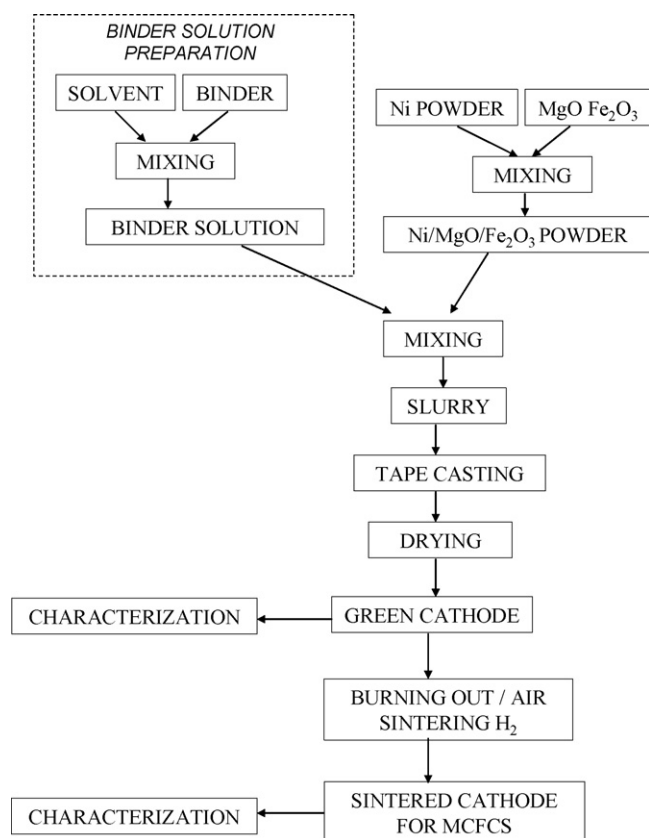
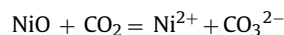


Fig. 1. Flowchart of the general production process of the Ni(Mg,Fe)O stabilized cathode.

fuel cell's performance. The rate of NiO dissolution is proportional to the partial pressure of CO₂ and may involve the following reaction:



The dissolution kinetics of NiO is also a function of the electrolyte basicity, and hence it depends on the cations present in the melt.

In order to solve the above problems, alternative materials which have lower dissolution rates, such as LiCoO₂ [2], LiFeO₂ [3] and Li₂MnO₃ [4], have been taken into account as MCFC cathodes.

In previous works the employment of cathodes such as Ni covered by lithium cobaltite precursors [5] (hereafter labelled

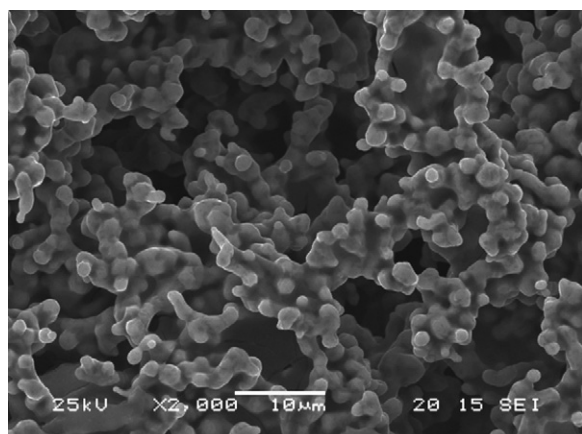


Fig. 2. SEM micrographs of Ni/Co-acetates cathode.

with Ni/Co-acetates) and a porous Ni doped with magnesium and iron oxides [6] (hereafter labelled with Ni(Mg,Fe)O) was investigated. Cathodes were prepared following procedures developed in ENEA's laboratories and characterized in morphology, electrochemical properties and conductivity.

The aim of the present work is to evaluate the prepared cathode materials in terms of cell performance and durability.

All the experiments were carried out in a 100 cm² fuel cell and the results were compared with a conventional Ni (INCO 255) cathode. Polarization curves and internal resistance (iR) measurements were carried out during the cell lifetime (1000 h) and the effect of gas composition variation on the cell performance was studied. A qualitative analysis of Ni dissolution was made by scanning electron microscopy (SEM) coupled with EDS-analysis (energy dispersive X-ray spectroscopy) on the active components after the in-cell test to evaluate the degradation and dissolution of the new cathode materials in molten carbonates.

2. Experimental

2.1. Cathode preparation

Ni/Co-acetates cathodes were prepared by means of a sol-gel process [7]. The starting sol used in complex sol-gel process was prepared adding LiOH to an aqueous solution of Co²⁺ acetate with ascorbic acid, then alkalized with aqueous ammonia to pH 8. In these sols, diluted with ethanol, porous Ni surface was dipped and withdrawn at a controlled rate several times, to achieve the required film thickness. To simplify electrode preparation, no thermal treatments to produce lithium cobaltite were made: during the cell start-up LiMg_{0.05}Co_{0.95}O₂ is obtained from the acetate precursors.

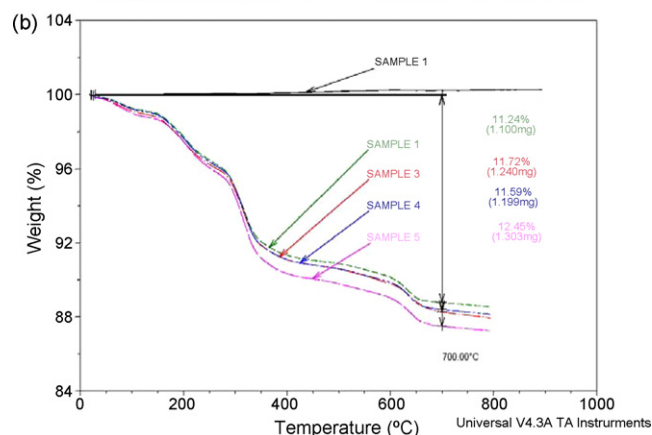
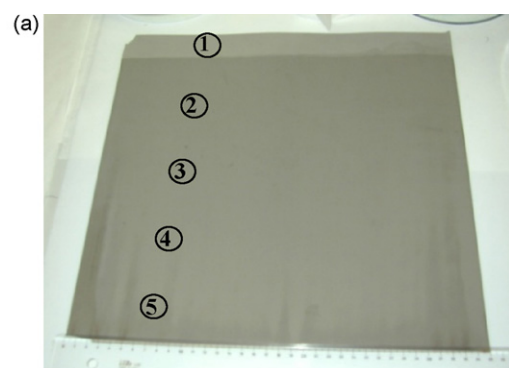


Fig. 3. (a) Picture of the 35 × 35 cm² sheet of Ni/Co-acetates cathode and (b) TGA curves of five different samples collected from Ni/Co-acetates cathode.

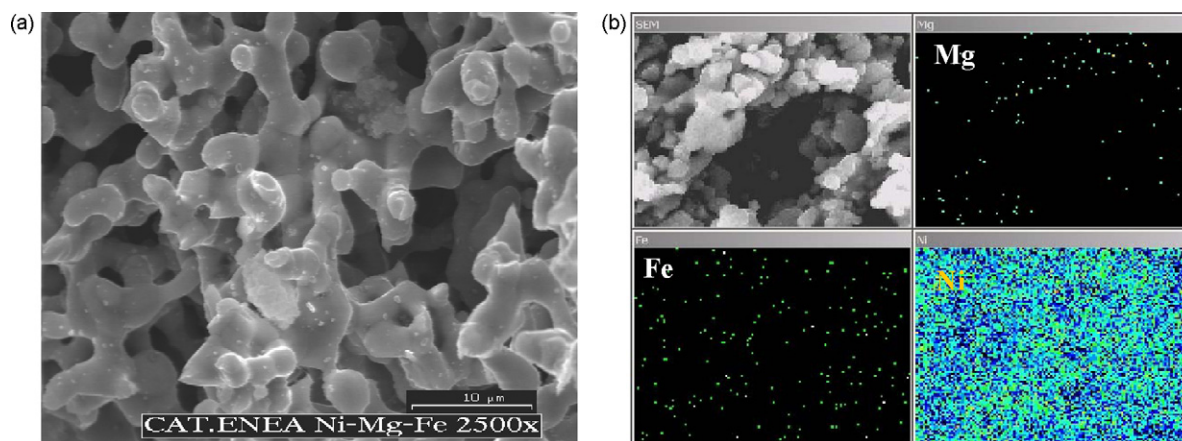


Fig. 4. (a) SEM micrographs of Ni(Mg,Fe)O cathode and (b) chemical mapping obtained by means of EDS analysis of Ni(Mg,Fe)O cathode.

The Ni(Mg,Fe)O cathode was made by a tape casting and sintering process (Fig. 1). A binder solution was mixed together with Ni, MgO and Fe₂O₃ powders and the resulting slurry was used in the tape-casting process. Two kinds of binders were tested: a traditional organic solvent soluble binder and a more environmentally friendly water-soluble binder. The test carried out using an aqueous binder gave a good flexible tape with 72% porosity and a thickness of 0.33 mm.

The obtained green cathode was dried slowly at room temperature and submitted to heat treatments to obtain Mg_{0.05}Fe_{0.01}Ni_{0.94}O. Afterwards the cathode was lithiated in-cell during the start-up step.

2.2. Cathode characterization

The materials prepared into cathodes were investigated by thermogravimetric analysis (TGA Instruments) in order to study the electrode structure and its homogeneity.

The cathode morphology before and after in-cell tests was examined by scanning electron microscopy (JEOL ISM 5510 LV) and EDS analysis (IXRF 500).

2.3. In-cell tests

The cathodes were tested in a 100 cm² surface area MCFC. The cell was assembled with a Ni–Cr alloy anode, a γ-LiAlO₂ matrix and a Li/K carbonate electrolyte (molar ratio 62:38). The results obtained from electrochemical tests were compared with those of a cell assembled with the commercial Ni (INCO 255) electrode.

The cell performance was studied at $T=650^{\circ}\text{C}$ and $P=1\text{ atm}$, for about 1000 h. The dependence of cell performance upon the cathodic gas composition was investigated by changing the partial pressure of O₂ and CO₂. Polarization curves were obtained by an electronic load (N333 Agilent). Current interruption technique was used to calculate the iR value and to correct the measured cell voltage for the ohmic potential drop. The initial fast change of the cell voltage when current is applied or interrupted, was recorded by a National Instruments acquisition card with an acquisition rate of 2000 samples s⁻¹. A custom compiled LabView program was used to control the acquisition.

3. Results and discussion

3.1. Cathode preparation and characterization

3.1.1. Ni/Co-acetates cathode

Fig. 2 shows a SEM image of the Ni/Co-acetates cathode prepared by means of the sol–gel process; it is worth noticing that the cathode keeps the typical porous structure of a commercial Ni cathode but there is also evidence of an amorphous layer covering the grains' surface.

Cathodes with an area of 35 × 35 cm² were prepared. To check homogeneity, five samples were collected from different points of the cathode sheet (Fig. 3a) and were investigated by means of TGA analysis (Fig. 3b). The results (Table 1) show that the cathode dis-

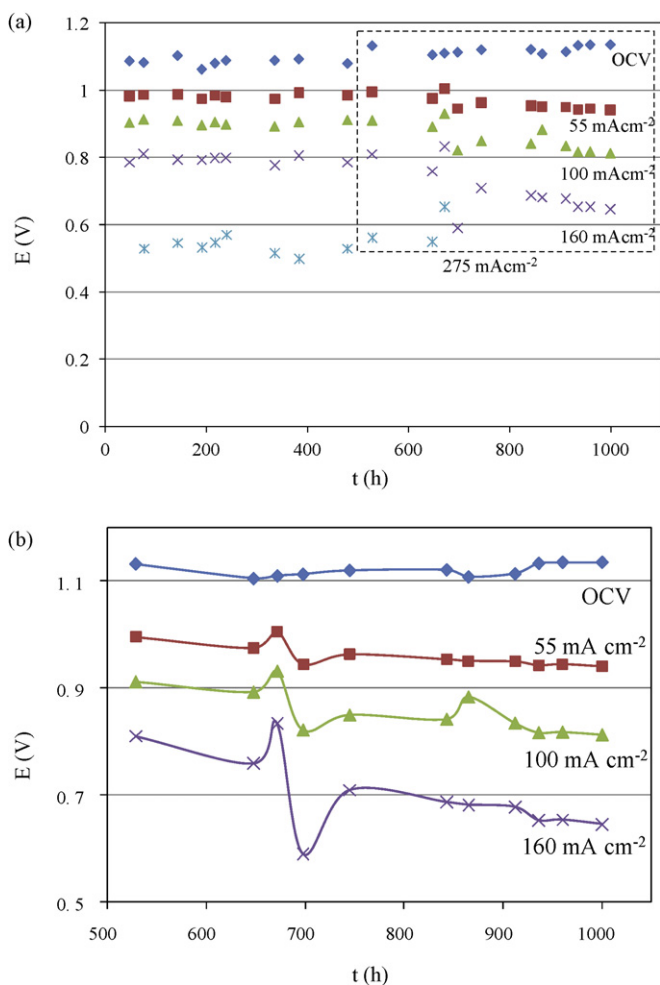


Fig. 5. (a) OCV and cell potential values at different current densities for Ni/Co-acetates as a function of time and (b) Detail.

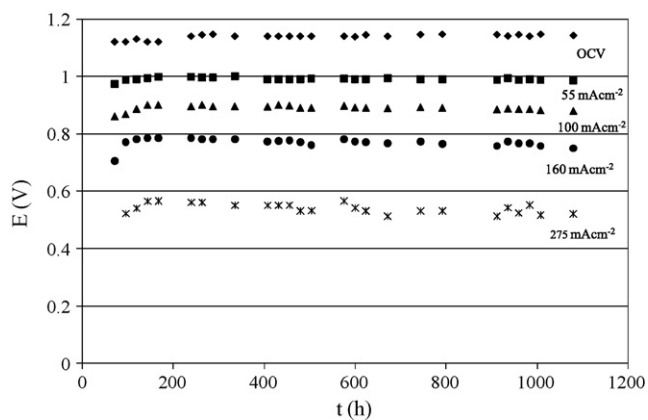


Fig. 6. OCV and cell potential values at different current densities, for Ni(Mg,Fe)O cathode, as a function of time.

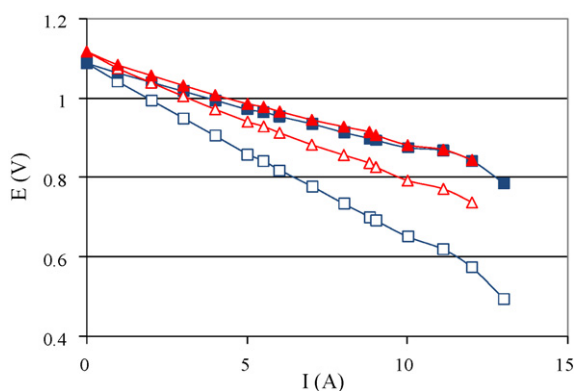


Fig. 7. Polarization curves: (Δ) before shut down, (▲) before shut down iR-corrected, (□) post shut down, (■) post shut down iR-corrected.

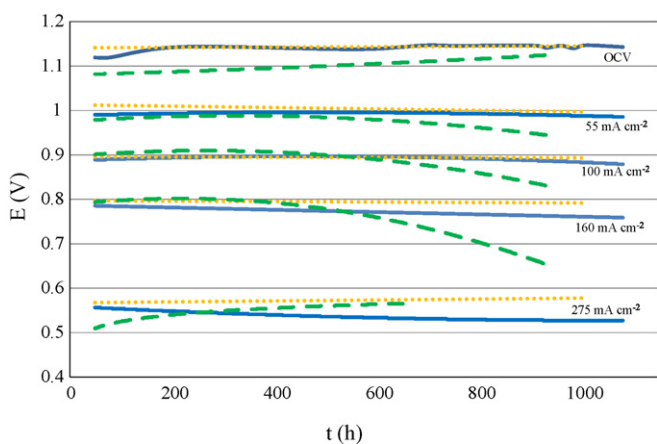


Fig. 8. Cell Voltage at different current densities as a function of time, comparison of trends for the three cathodes: “dotted line” NiO cathode, “broken line” Ni/Co-acetates and “unbroken line” Ni(Mg,Fe)O cathode.

Table 1
TGA analysis results and LiCoO₂ precursors present on Ni/Co-acetates cathode.

Sample	Weight loss (%)	LiCoO ₂ amount (%)
2	11.24	1.37
3	11.72	1.44
4	11.59	1.42
5	12.45	1.54

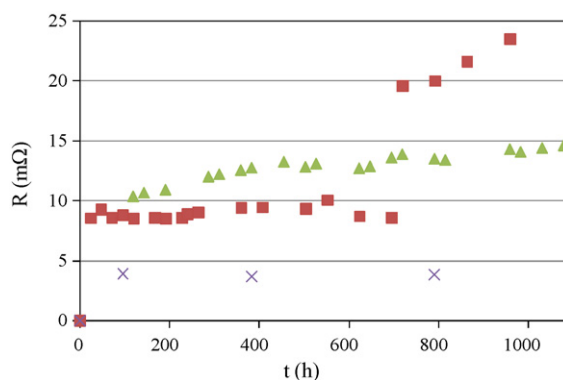


Fig. 9. Resistance values for the cathodes as a function of time: (■) Ni/Co-acetates, (×) NiO and (▲) Ni(Mg,Fe)O.

plays a homogenous deposition of lithium cobaltite precursors on the surface except for the edges.

3.1.2. Ni(Mg,Fe)O cathode

In Fig. 4aa SEM micrograph of the Ni(Mg,Fe)O cathode, at 2500× magnification, is reported showing that the main porous structure of the Ni cathode is preserved. Chemical mapping obtained by means of EDS analysis (Fig. 4b) shows that Mg and Fe oxides are homogeneously spread into the cathode.

3.2. In-cell tests

To investigate cell performance, polarization curves were carried out during the cell lifetime (about 1000 h).

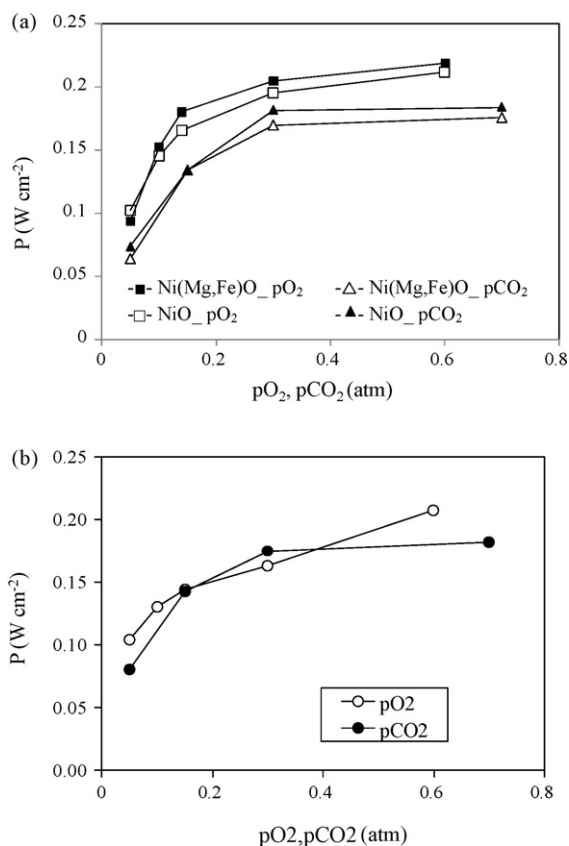


Fig. 10. Dependency of cell power on pO₂ (pCO₂ kept at 0.3) and pCO₂ (pO₂ kept at 0.14): (a) Ni(Mg,Fe)O and (b) Ni/Co-acetates.

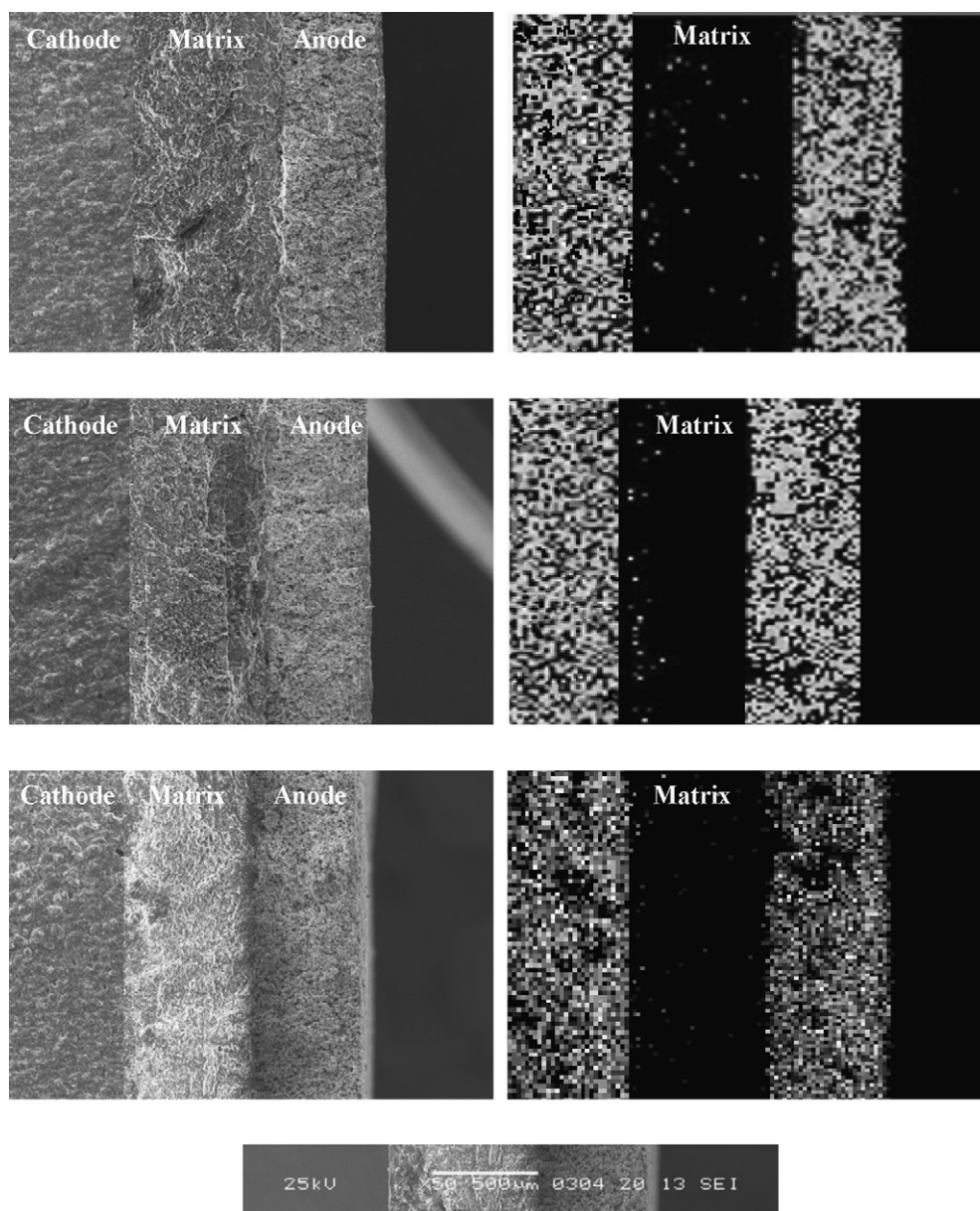


Fig. 11. EDS mapping for Ni element of the cathode/matrix/anode package cross-section for (a) NiO, (b) Ni(Mg,Fe)O and (c) Ni/Co-acetates.

The OCV and cell potential at different current density values as a function of time for the Ni/Co-acetates cell and for the Ni(Mg,Fe)O cell are shown in Fig. 5 and in Fig. 6, respectively. The Ni(Mg,Fe)O cell performance was stable for all the investigated current densities showing high potential values.

The performance of the Ni/Co-acetates cell displays a potential drop around 700 h (Fig. 5b) due to an unforeseen shut down of the plant: this resulted in a rise in resistance from 8.7 to 23 m Ω . The latter high value of internal resistance can probably be referred to detachments in the microstructure among the active components. In fact, this evidence is also confirmed in Fig. 7 where polarization curves are reported before and after the shut down with and without the internal resistance (iR) correction. The accident did not invalidate electrochemical performance: the polarization curves, corrected for iR, overlap exactly.

Fig. 8 shows a comparison among the three cathodes: the dotted line represents the NiO cathode, the broken line the Ni/Co-acetates cathode and the unbroken line the Ni(Mg,Fe)O cathode. Trends are similar in spite of the very different iR values for each cell: close to 5 m Ω for NiO, 15 m Ω for Ni(Mg,Fe)O and from 8.7 to 23 m Ω for

Ni/Co-acetates (Fig. 9). R values are very different but their effect on potential values is negligible.

Finally, in order to study the effect of gas composition variation on the cell performance of Ni(Mg,Fe)O and Ni/Co-acetates, measurements of cell potential at different partial pressures of O₂ (p_{O_2}) and CO₂ (p_{CO_2}) were carried out. The dependency of cell power on p_{O_2} and p_{CO_2} is similar in both cathodes (Fig. 10): the electrochemical cell performance increases as the oxygen and carbon dioxide partial pressures increase indicating a positive effect on the cathodic reaction. For NiO and Ni(Mg,Fe)O cells a plateau seems to be reached both for p_{CO_2} and p_{O_2} higher than 0.4 atm; on the contrary for the Ni/Co-acetates cell a small increase of the power value seems present also for O₂ values higher than 0.4 atm.

3.3. Post-test analysis

The amount of Ni precipitated in the tile was investigated qualitatively by SEM micrographs and corresponding EDS Ni mapping of the cathode/matrix/anode package cross-section (Fig. 11). In the

figure a cross-section of the cell assembly is shown where the two electrodes and the alumina tile in the middle are well evidenced.

For the Ni(Mg,Fe)O cell (Fig. 11b) the presence of Ni is evident at the interface between tile and cathode side. Ni concentration inside the matrix is lower than for the NiO cell (Fig. 11a) and limited to the cathode/matrix interface. The result can be explained by a lower Ni precipitation rate for Ni(Mg,Fe)O cathode probably related to the formation of a solid solution between Ni and Fe, which is insoluble in molten carbonates and protects the cathode from Ni dissolution.

From a comparison between the NiO cell and Ni/Co-acetates cell (Fig. 11c) it is possible to see that the amount of Ni scattered into the tile is lower for the cathode protected with a thin layer of lithium cobaltite doped with magnesium ($\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$).

4. Conclusions

The issue of NiO dissolution in a Li/K eutectic carbonates melt was examined by investigating the effects of additives in the preparation of conventional Ni cathodes and the effect of covering the Ni substrate with a thin layer of lithium cobaltite doped with magnesium.

A Ni electrode covered with a thin layer of lithium cobaltite doped with Mg ($\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$) was fabricated by complex sol-gel process and a porous nickel/magnesium oxide/iron oxide

($\text{Mg}_{0.05}\text{Fe}_{0.01}\text{Ni}_{0.94}\text{O}$) cathode was made by tape casting and sintering.

New Ni-based electrodes were characterized in terms of chemical-physical properties by thermal analysis whereas the cathode morphology before and after in-cell testing was examined by scanning electron microscopy and EDS mapping.

After in-cell tests, from a comparison with untreated NiO, it can be observed that the two alternative cathode materials have similar performance and show a good potential stability during the cell operating time. From the post-test analysis the Ni(Mg,Fe)O and Ni/Co-acetates cathodes seem to succeed in reducing Ni dissolution.

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