



*The Abdus Salam
International Centre for Theoretical Physics*



2245-3

**Joint ICTP-IAEA Advanced School on the Role of Nuclear Technology
in Hydrogen-Based Energy Systems**

13 - 18 June 2011

Neutron diffraction studies of electrodes for innovative fuel cells of industrial interest

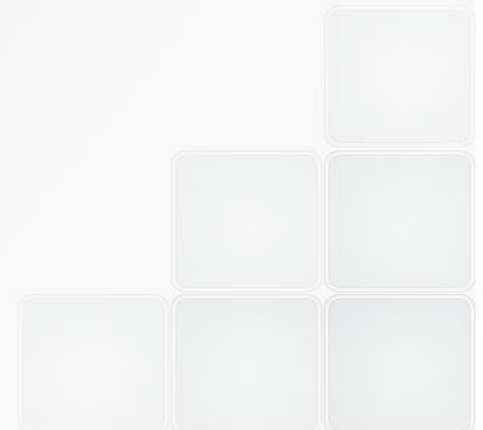
Roberto Coppola
*ENEA Centro Ricerche della Casaccia
Roma
Italy*



Neutron diffraction studies of electrodes for innovative fuel cells of industrial interest

ICTP EC School "Development and characterisation of materials for hydrogen based energy systems: role of nuclear technology" 13-18/6/2011

Roberto Coppola, ENEA-Casaccia, Roma – I



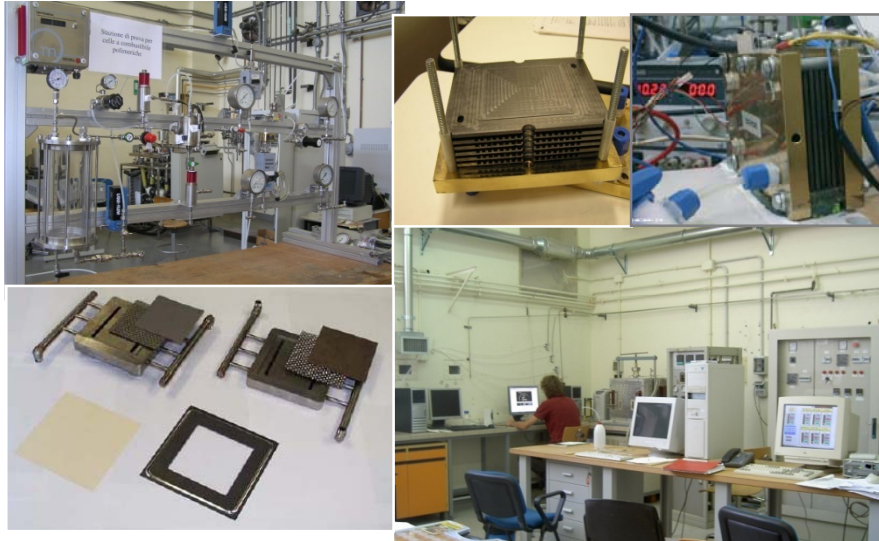
Hydrogen activities in ENEA

- **Hydrogen production**
Fossil fuels (NG, coal) and renewable sources (thermal solar, biomass)
- **Hydrogen storage**
Metal and chemical hydrides
- **Hydrogen utilization**
Fuel cells and advanced thermal cycles



Technical and socio-economic studies to evaluate the prospects of hydrogen and related technologies

Fuel cell activities in ENEA



Fuel cell activities, started in the early 1980s, are focused on the development and demonstration of:

- ◆ polymer electrolyte fuel cells for stationary and transport application
- ◆ molten carbonate fuel cells for on-site and distributed generation

Research activities on solid oxide fuel cells are also carried out

POLYMER ELECTROLYTE FUEL CELLS

- R&D of innovative materials and components
- Stack development and cell configuration
- Demonstration of 1-5 kW stacks and systems
- Development and testing of fuel processors operating with different fuel (NG, GPL) to integrate with PEFC units

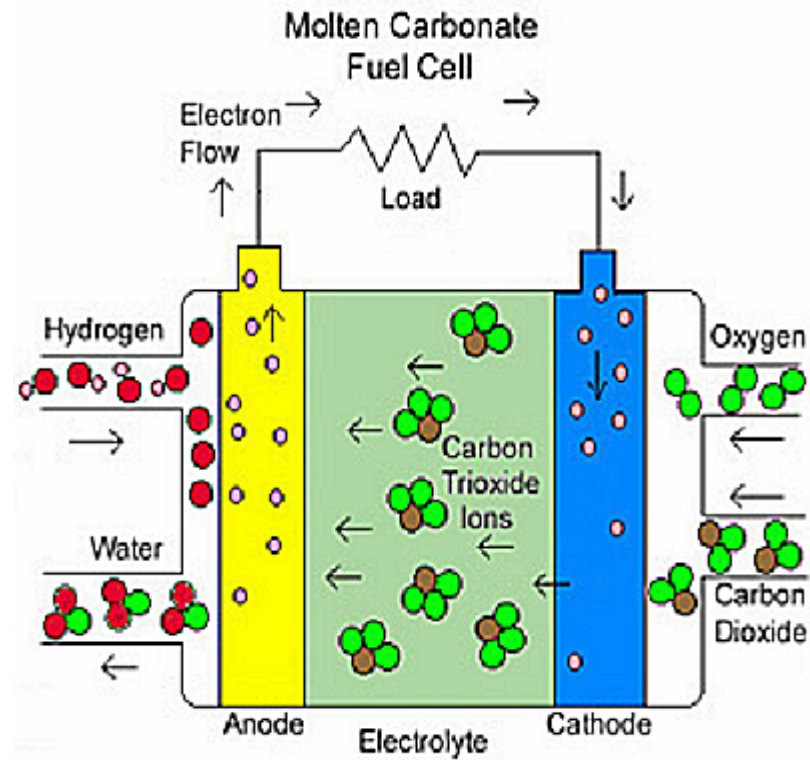
MOLTEN CARBONATE FUEL CELLS

- R&D of innovative materials and components
- Development of hybrid systems (MCFC – gas turbine)
- Development and operation of MCFC systems fuelled with different fuels (NG, biofuel, syngas, etc)

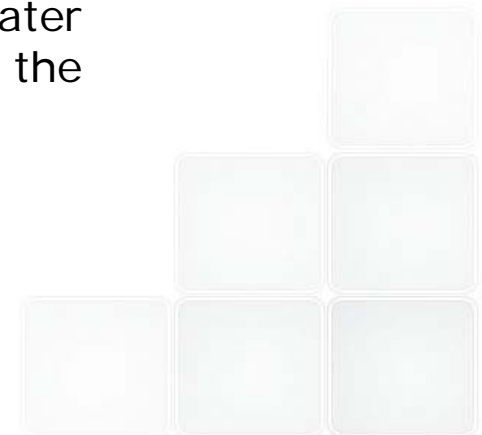
MAIN COLLABORATIONS



CNR Institutes and Universities

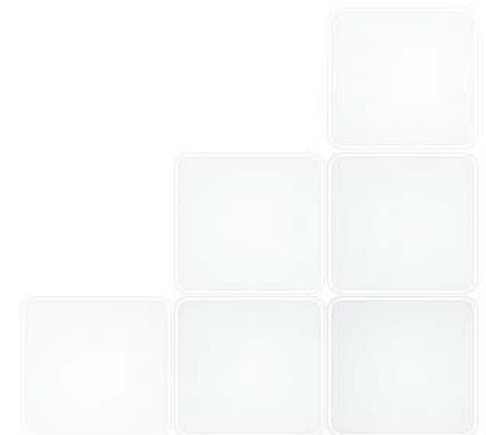


Scheme of a molten carbonate fuel cell, where the electrolyte is a combination of alkali carbonates, water is produced at the anode site and CO_2 is needed at the cathode site.



IRMATECH PROJECT

**"Forming, sintering, characterization of
Mg-LiCoO₂ / NiO cathodes"**

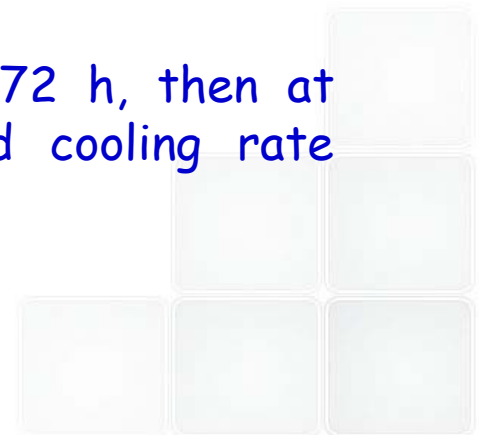


Preparation of nickel oxide cathodes coated with a layer of lithium cobaltite doped with magnesium

The substrate for deposition was supplied by AFCO in the form of A4 sheets of porous metallic nickel of about 0.5 mm of thickness. The substrate is partially oxidized (30%) in air at 600 °C for 1 h.

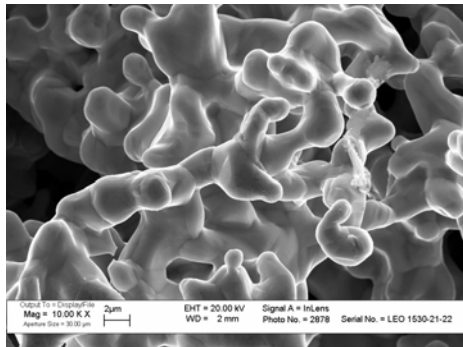
The starting sol used in Complex Sol-Gel Process (CSGP) have been prepared by adding LiOH to aqueous acetates solution of Co 2+ with ascorbic acid, then alkalizing with aqueous ammonia to pH=8. In these sols, diluted with ethanol, porous cathodes plates have been dipped and withdrawn at controlled rate several times to achieve a desiderate film thickness.

The coated substrates were soaked at 200° C for 72 h, then at 400° C for 1h and calcined (using low heating and cooling rate 1° C/min) at 650° C up to 4 h.

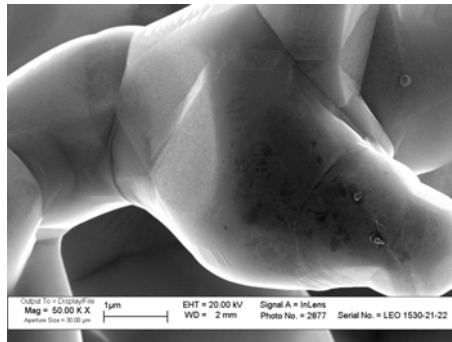


Characterization of nickel oxide /lithium cobaltite electrode. Electron scanning microscopy

(a)

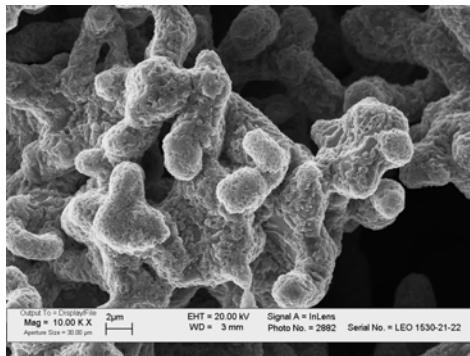


(b)

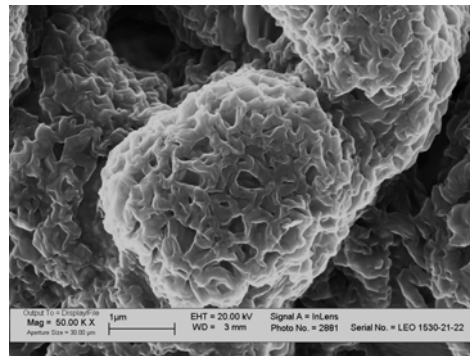


FE-SEM micrographs of as received porous metallic nickel sheet supplied by AFCO for coating with lithium cobaltite (a) 10.000 X. and (b) 50.000 X

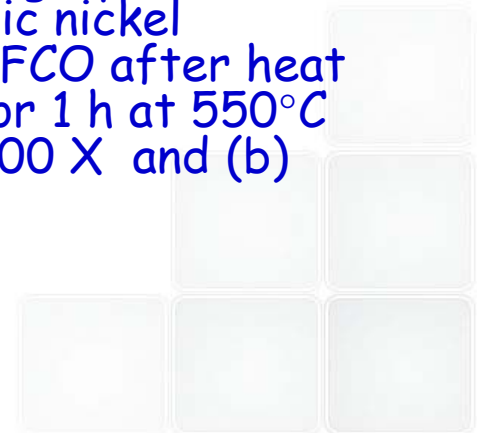
(a)



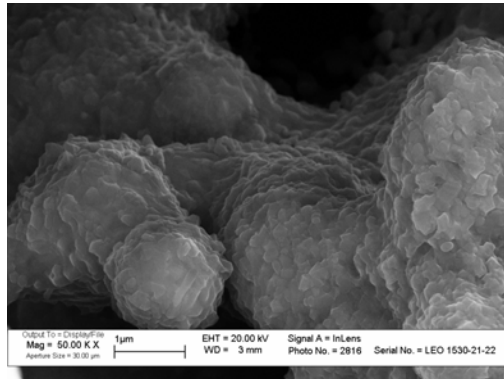
(b)



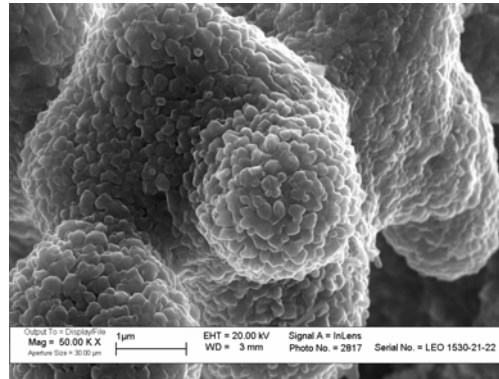
FE-SEM micrographs of porous metallic nickel supplied by AFCO after heat treatment for 1 h at 550°C in air (a) 10.000 X and (b) 50.000 X.



(a)

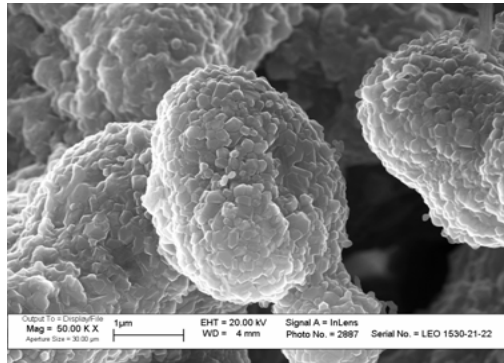


(b)

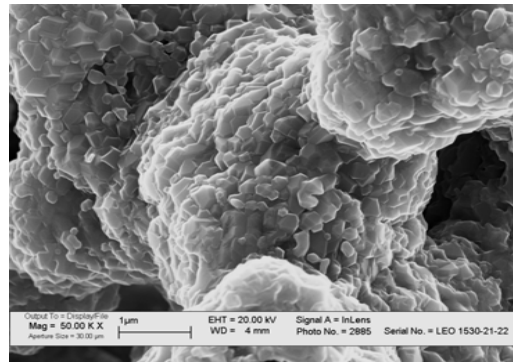


FE-SEM micrographs representing the nickel oxide covered with lithium cobaltite doped with magnesium electrode: (a) intra - pore deposition, (b) superficial deposition.

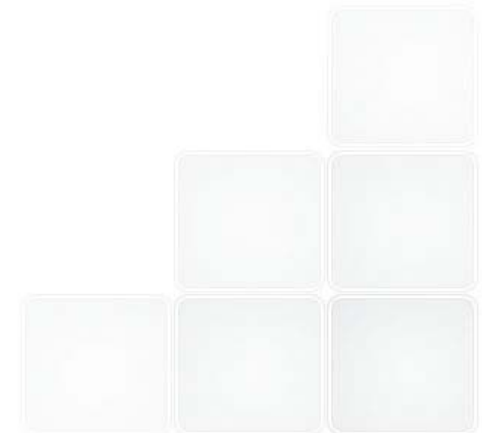
(a)

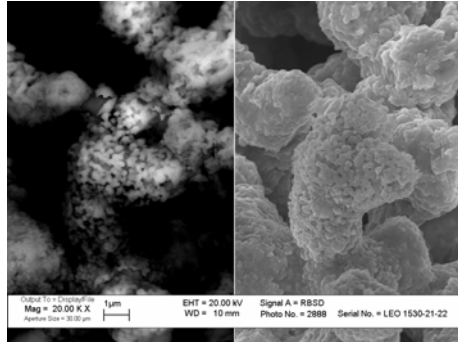


(b)

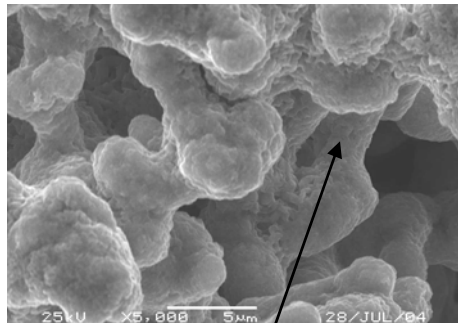


FE-SEM micrographs representing the nickel oxide covered with lithium cobaltite electrode cross section: (a) external surface, (b) internal.

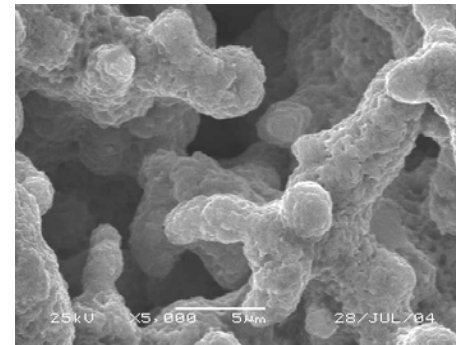




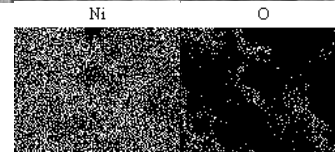
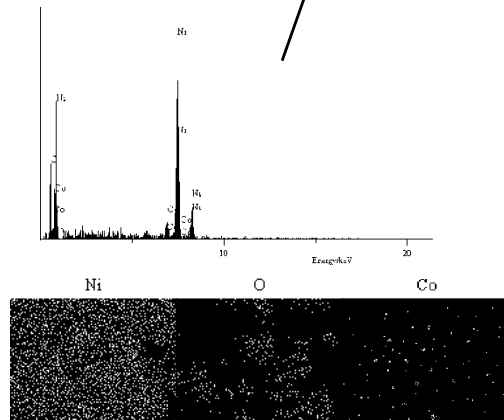
FE-SEM micrographs representing the nickel oxide covered with lithium cobaltite electrode. Backscattering image on the left.



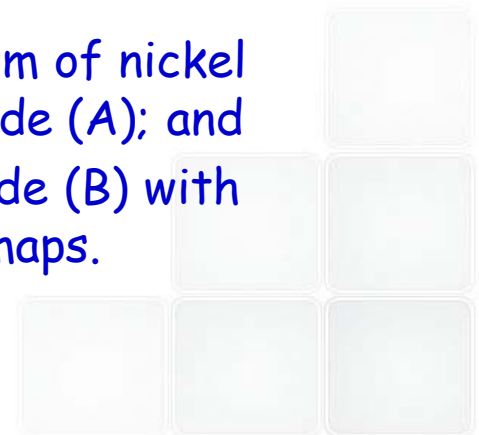
(A)



(B)



SEM pictures and EDS spectrum of nickel oxide/lithium cobaltite electrode (A); and partially pre-oxidised Ni cathode (B) with their corresponding elements maps.

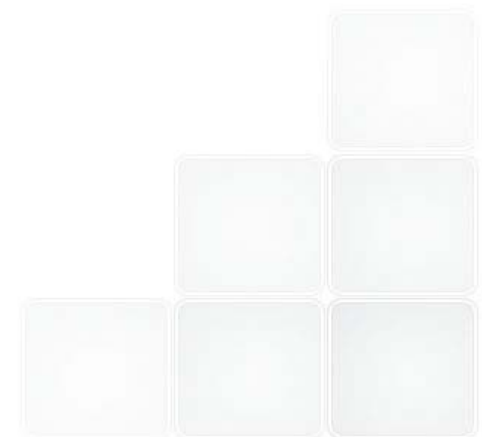


Porosimetry

Pore size distribution in NiO/Mg-LiCoO₂ cathodes was investigated by mercury porosimetry.

The coating of nickel oxide with lithium cobaltite slightly changes the pore structure of the electrode.

The total sample porosity decreases from 67.15% to 60.28%.



Electrical conductivity of cathodes

The electrical conductivity of cathodes was measured by a d.c. technique following the Van der Pauw method in the temperature range 500°C ÷ 850°C, as a function of gas composition and time.

- Conductivity measurements were carried out on three different electrodes:
- . a conventional porous nickel sheet (supplied by AFCO) partially oxidized (30%) and coated with Mg-doped lithium cobaltite
 - . a bulk Mg-doped lithium cobaltite on which were previously carried out chemical, physical and electrochemical characterizations.
 - . a 30% nickel oxide electrode coated with Mg-doped lithium cobaltite .

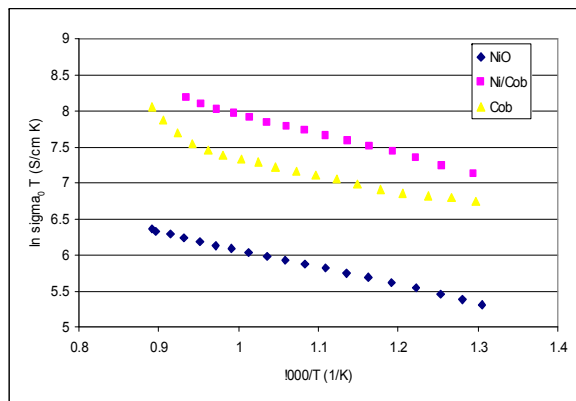
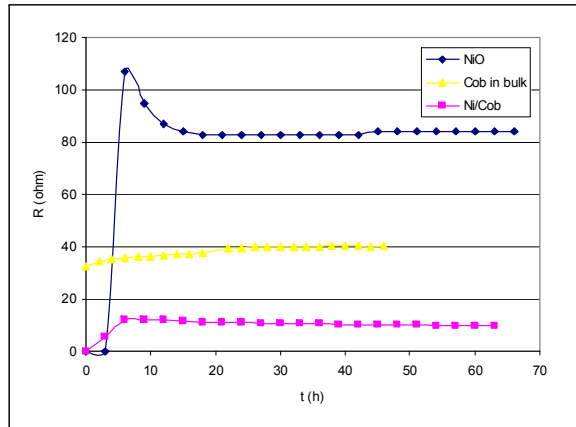
The conductivity σ (S cm⁻¹) is defined as $1/\rho$, where ρ (Ω cm) is the specific resistivity of the specimen measured by the van der Pauw method. According to this method the specific resistivity is given by the following equation:

$$\rho = \frac{h\pi}{\ln 2} \frac{(R_a + R_b)}{2} \frac{f R_a}{R_b}$$

To compare the electrical conductivity of materials with different porosity, the measured conductivity was converted to the specific conductivity (conductivity at theoretical density) using the semi empirical relationship

$$\sigma_0 = \sigma (1-P)^{-1.75}$$

where σ is the measured electrical conductivity, σ_0 is the specific electrical conductivity and P is the porosity fraction.



Electrical resistance as a function of time in air of nickel oxide, nickel oxide covered by lithium cobaltite and lithium cobaltite .

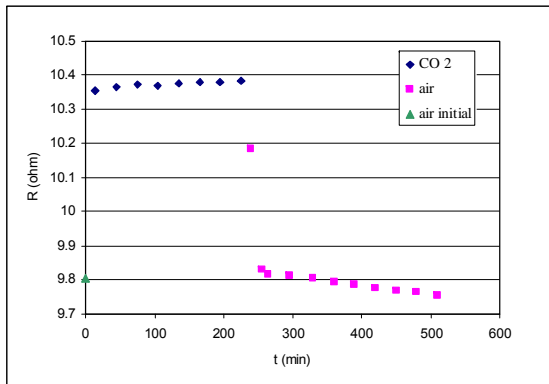
Nickel oxide shows a resistance of 85 ohm, higher than that of lithium cobaltite (40 ohm) and nickel oxide coated with lithium cobaltite (10 ohm). The reason for this behaviour is the absence of lithium ions intercalation which induces strong p-type semiconductor properties in the compound and increases conductivity significantly.

Arrhenius plot for the electrical conductivity in air of nickel oxide, nickel oxide covered by lithium cobaltite and lithium cobaltite .

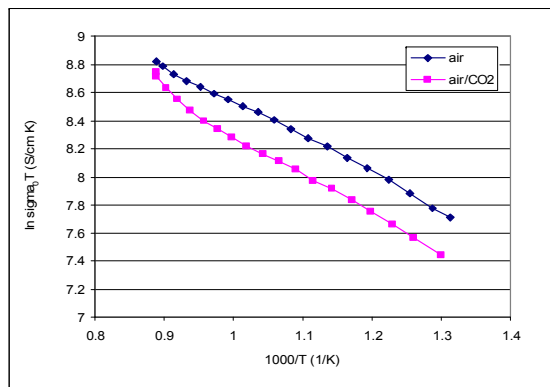
	E_a (eV)	$\ln \sigma_0$
NiO	0.21	8,5
NiO / Mg-LiCoO ₂	0.24	10,8
Mg -LiCoO ₂	0,18	9,4

Activation energy values for NiO, NiO / Mg-LiCoO₂, Mg -LiCoO₂

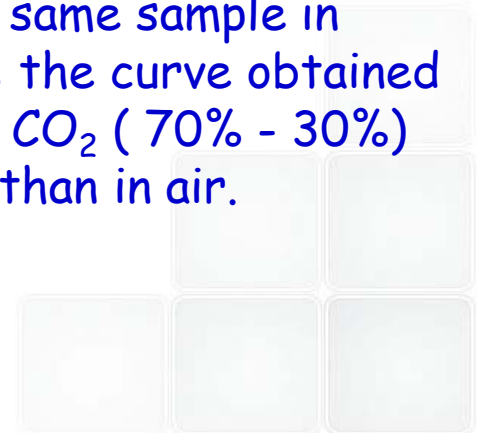
Effect of CO_2 on nickel oxide/Mg- lithium cobaltite electrode, $T=650^\circ C$.



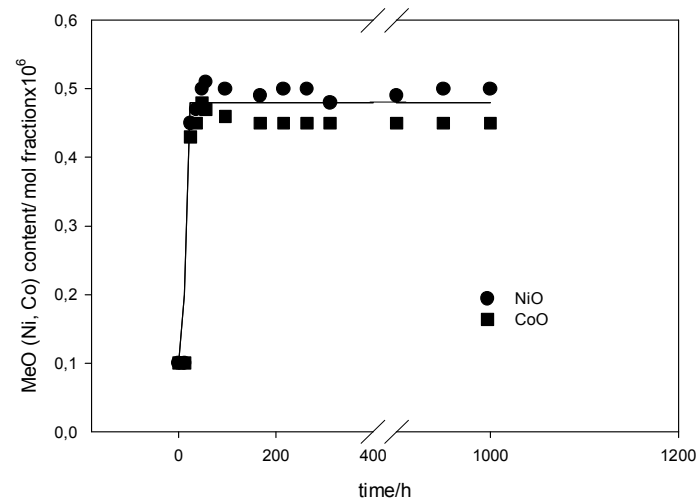
A fast change of the electronic conductivity on NiO/Mg-LiCoO₂ was observed in CO₂ atmosphere. Probably a selective interaction of CO₂ on active sites used for the hopping of the charge carriers took place, with the consequence to block the conduction mechanism. If air atmosphere is fluxed again, resistance decreases to the initial value that means the reaction mechanism is reversible.



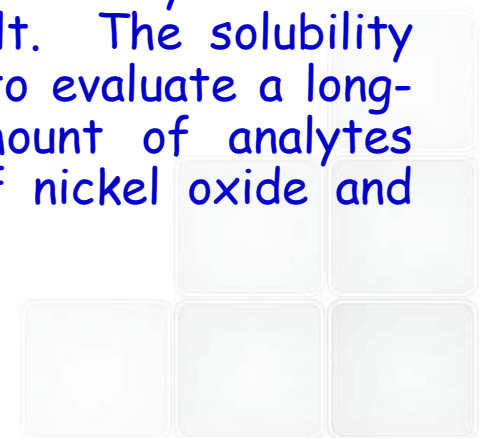
Arrhenius plots obtained for the same sample in different atmosphere are shown: the curve obtained in a mixed atmosphere of air and CO₂ (70% - 30%) shows a conductivity value lower than in air.



Cathode solubility



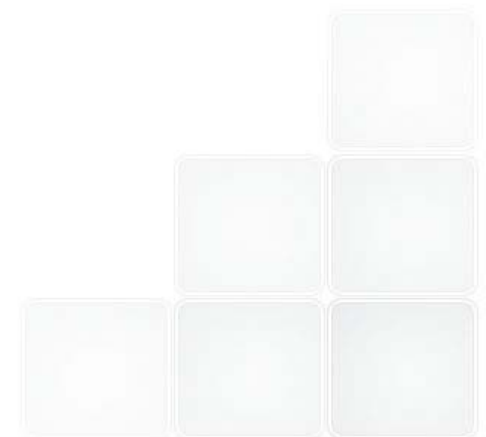
Time-dependence curve of the solubility in $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3 = 62/38$ mixtures at 650°C and $\text{PO}_2/\text{PCO}_2 = 0.33/0.67$ when nickel oxide/Mg-lithium cobaltite cathodes were immersed into the melt for 1000 h. The solubility has been expressed in terms of NiO and CoO content in the melt. The solubility measurements were carried out for long time in order to evaluate a long-term coating resistance. As it can be seen the amount of analytes concentration after 1000 h are well below the values of nickel oxide and lithium cobaltite solubility, namely 20 and 6 mol ppm.

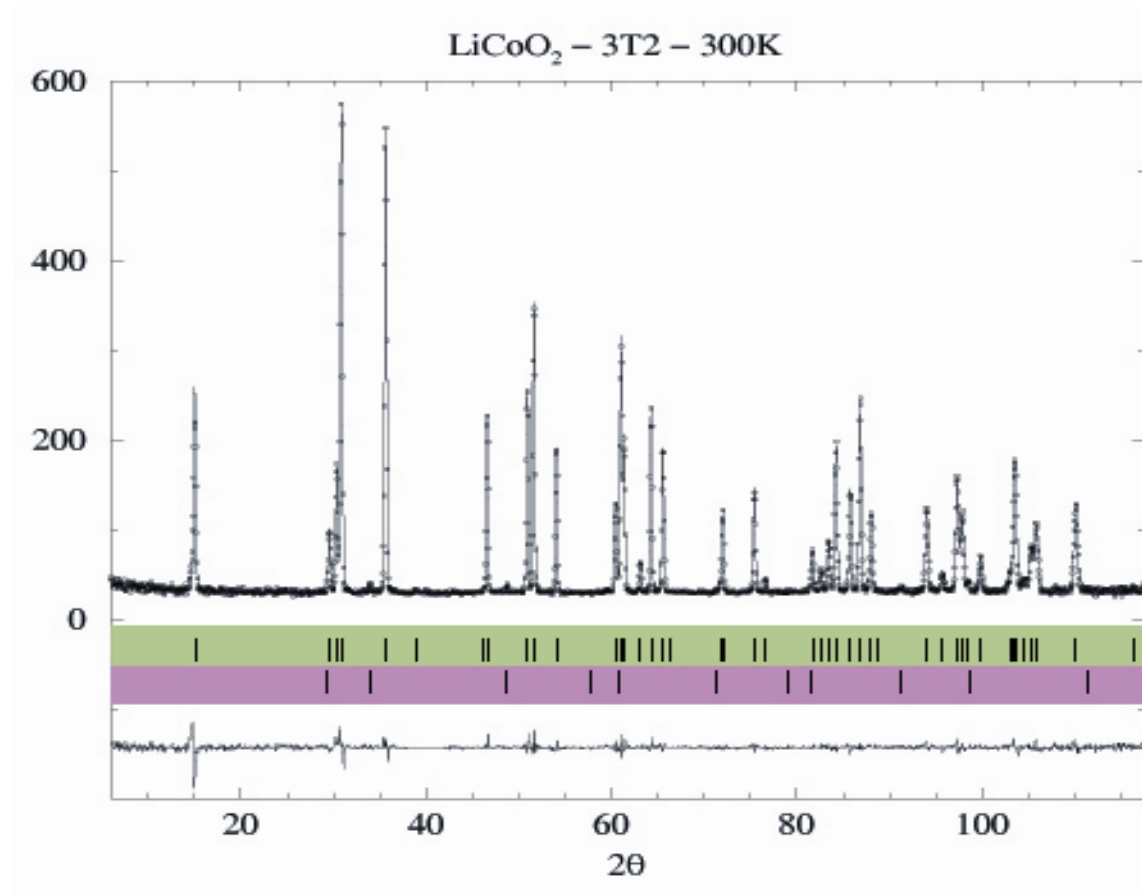


Neutron diffraction studies of LiCoO_2 synthesized by solid state reaction from carbonate precursors and doped with Mg

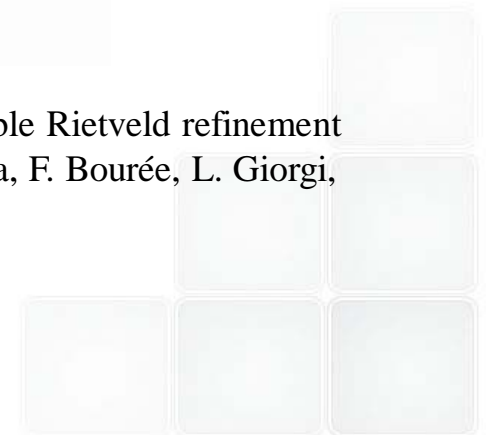
These measurements were carried out at LLB-Saclay both at RT and at 650°C

Double Rietveld refinement shows that Mg partly replaces Co in octahedral (3b) site and partly precipitates as MgO





Neutron diffraction study of standard LiCoMgO₂ (carried out at LLB-Saclay). The double Rietveld refinement (the two series of markers) allows to identify the presence of the MgO phase R. Coppola, F. Bourée, L. Giorgi, *PhysicaB* 276-278 (2000) 862



NEUTRON DIFFRACTION STUDY OF Ni/NiO ELECTRODES COATED WITH LiCoMgO₂

INVESTIGATED SAMPLES

Ni substrate

Ni/NiO substrate

Tape cast LiCoMgO₂ cobaltite (in the electrode the cobaltite is deposited by sol-gel)

As-received electrode

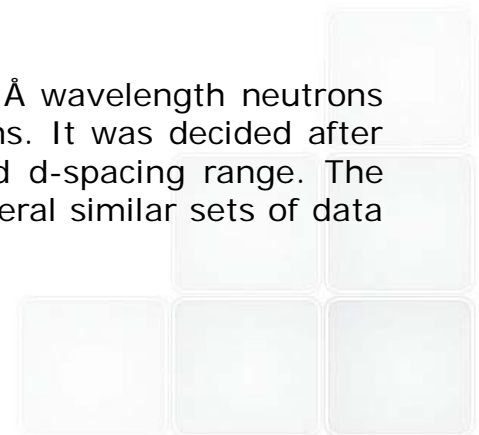
Electrode tested 100h at 650°C in the cell

In order to optimise the cobaltite diffracting volume, 40 pieces approx 2 cm² in size were stacked together

The measurements were carried out at the D20 diffractometer at the ILL-Grenoble

In the cases where the samples were in the form of strips, two different data collection strategies were used. The first involved mounting the strips in bundles with the individual strips parallel to the incoming neutron beam and the second with the strips aligned perpendicular to the beam. This allowed the effects of preferred orientation of the deposited material to be probed.

The set-up of the instrument was varied in the initial test between high-flux 2.4 Å wavelength neutrons and 1.3 Å wavelength neutrons to determine the optimal data collection conditions. It was decided after the initial tests that the 1.3 Å set-up provided the best combination of flux and d-spacing range. The sample slit settings and collimation were also varied during the tests to obtain several similar sets of data to determine the optimal set-up for any future experimental proposal.



D20 a High Flux Powder diffractometer @ ILL



monochromators

take-off angle 2θ	HOPG (002)		Cu (200)	
	$\lambda/\text{\AA}$	$\phi/n \text{ cm}^{-2} \text{ s}^{-1}$	$\lambda/\text{\AA}$	$\phi/n \text{ cm}^{-2} \text{ s}^{-1}$
26°	-	-	0.82	3.4×10^7
28°	-	-	0.88	4.5×10^7
30°	-	-	0.94	5.9×10^7
42°	2.41	4.2×10^7	1.30	9.8×10^7

take-off angle 2θ	Ge(113)				
	(115) $\lambda/\text{\AA}$	(117) $\lambda/\text{\AA}$	(119) $\lambda/\text{\AA}$	(337) $\lambda/\text{\AA}$	(335) $\lambda/\text{\AA}$
65°	1.17	0.85	-	-	-
90°	1.54	1.12	0.88	0.98	1.22
120°	1.88	1.37	1.07	1.20	1.49
$\omega_M/^\circ$	9	14	16	-6	-15

monochromator	geometry	vertical focus	take-off	reflections
Cu(200)	transmission	fixed	26-30°	200
Cu(200)	transmission	fixed	42-46°	200
HOPG(002)	reflection	fixed	42-46°	002
Ge(113)	reflection	variable	63-120°	hhl

collimation

primary collimation α_1	natural 27' Soller collimators 10'/20'
secondary collimation α_2	adjustable slits between monochromator and sample
mono-sample distance.	3.2 m
sample-detector dist.	1.47 m
max. beam size at sample	30 mm w x 50 mm h

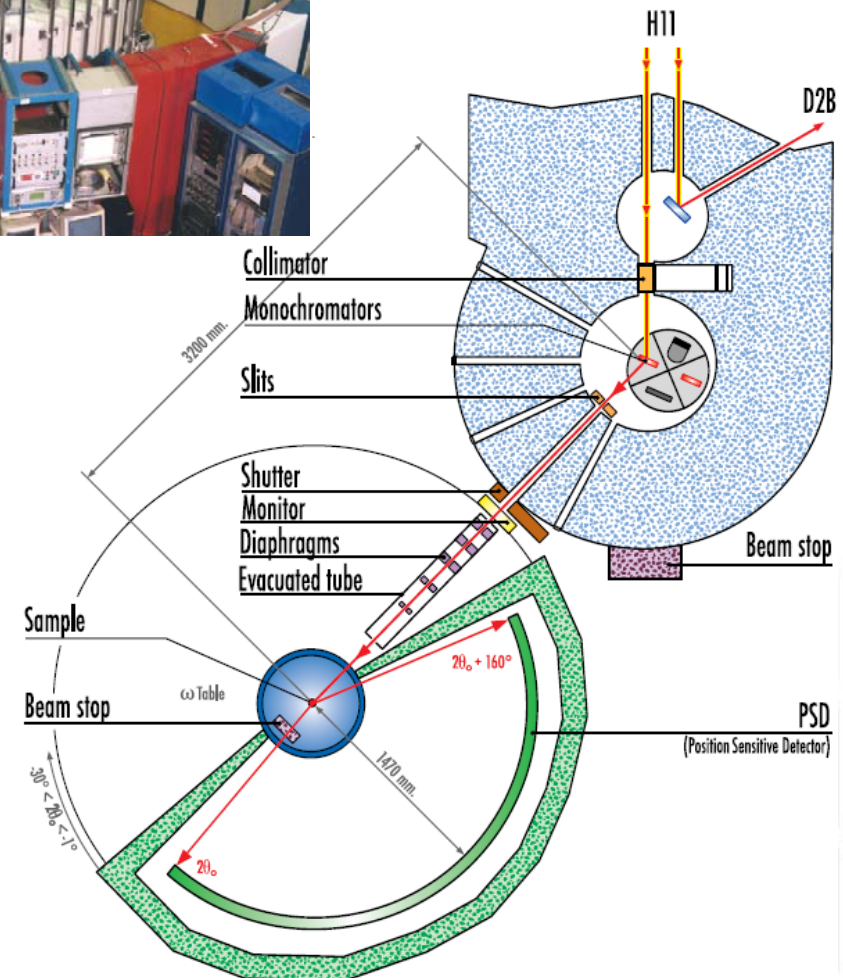
dedicated sample environment

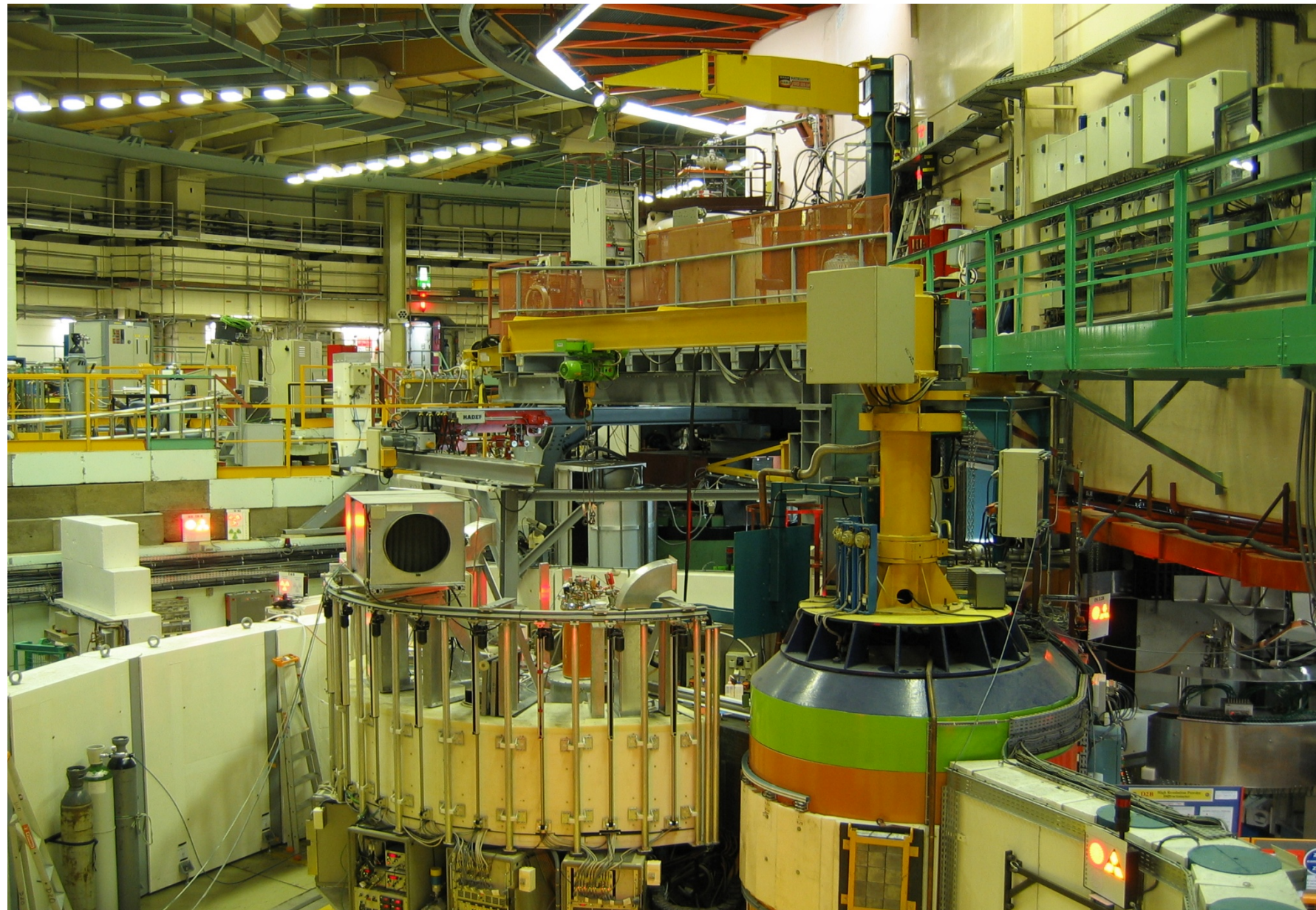
sample space - 750 mm diameter x 500 mm height	
sample environment	uses
vacuum vessel (620 mm diam.)	RT experiments
orange cryostat with V tail	1.7 - 300 K
furnace (V heater)	< 1150 C
furnace (Nb heater - background!)	< 1500 C
eulerian cradle	RT texture experiments
xy translator (250 mm)	RT strain experiments

D20 ... the most versatile and highest flux

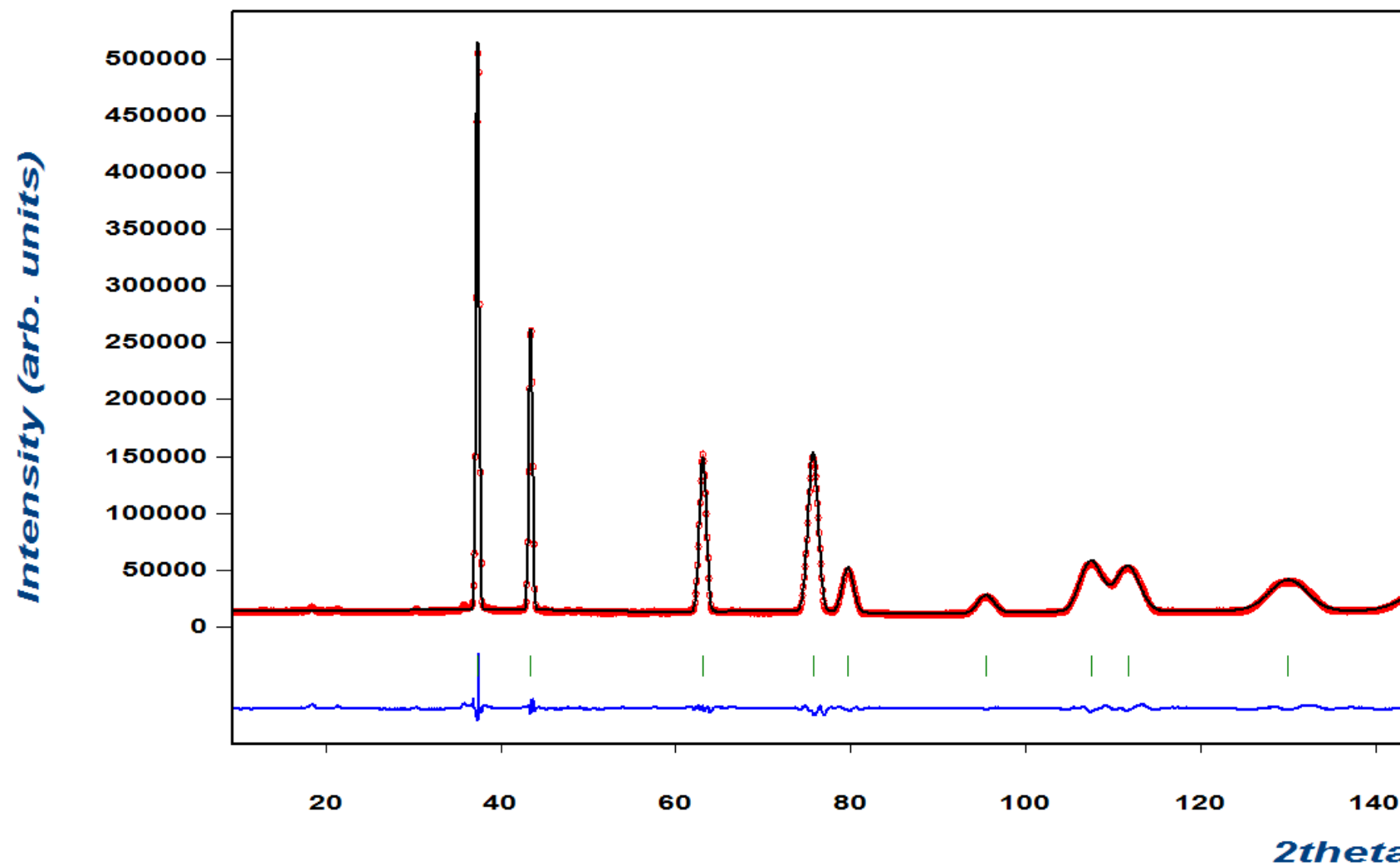
^3He microstrip gas-detector (PSD)

angular range in 2θ	153.6°
number of detection cells	1536
sample-detector distance	1.471 m
detector height	0.15 m

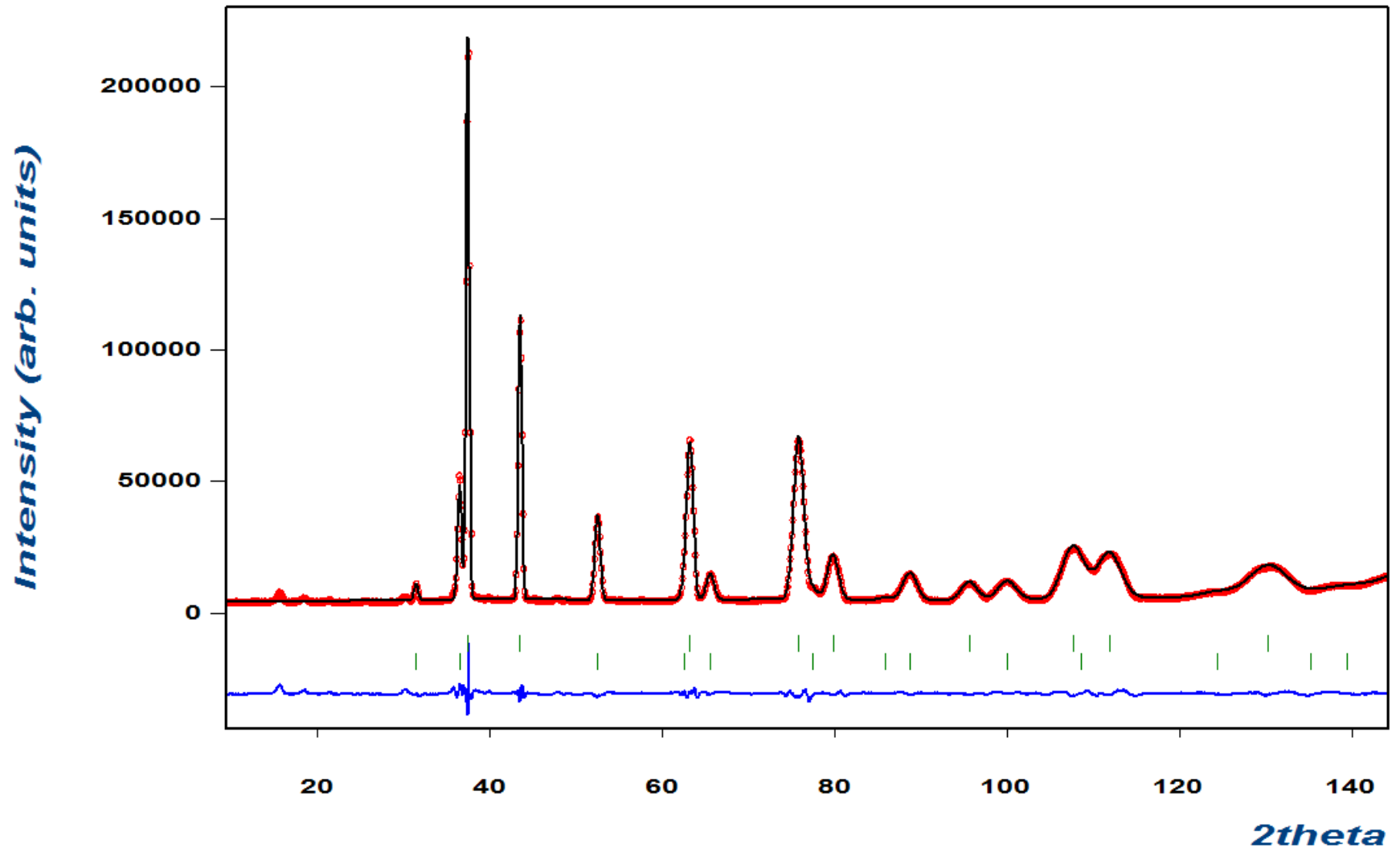




Pure Ni substrate perpendicular to beam 1.3 Å full beam



NiO deposited substrate strips perpendicular to beam 1.3 Å



LiMg_xCo_{1-x}O₂

=> Bragg R-factor: 8.75%, R_f-factor= 4.63%

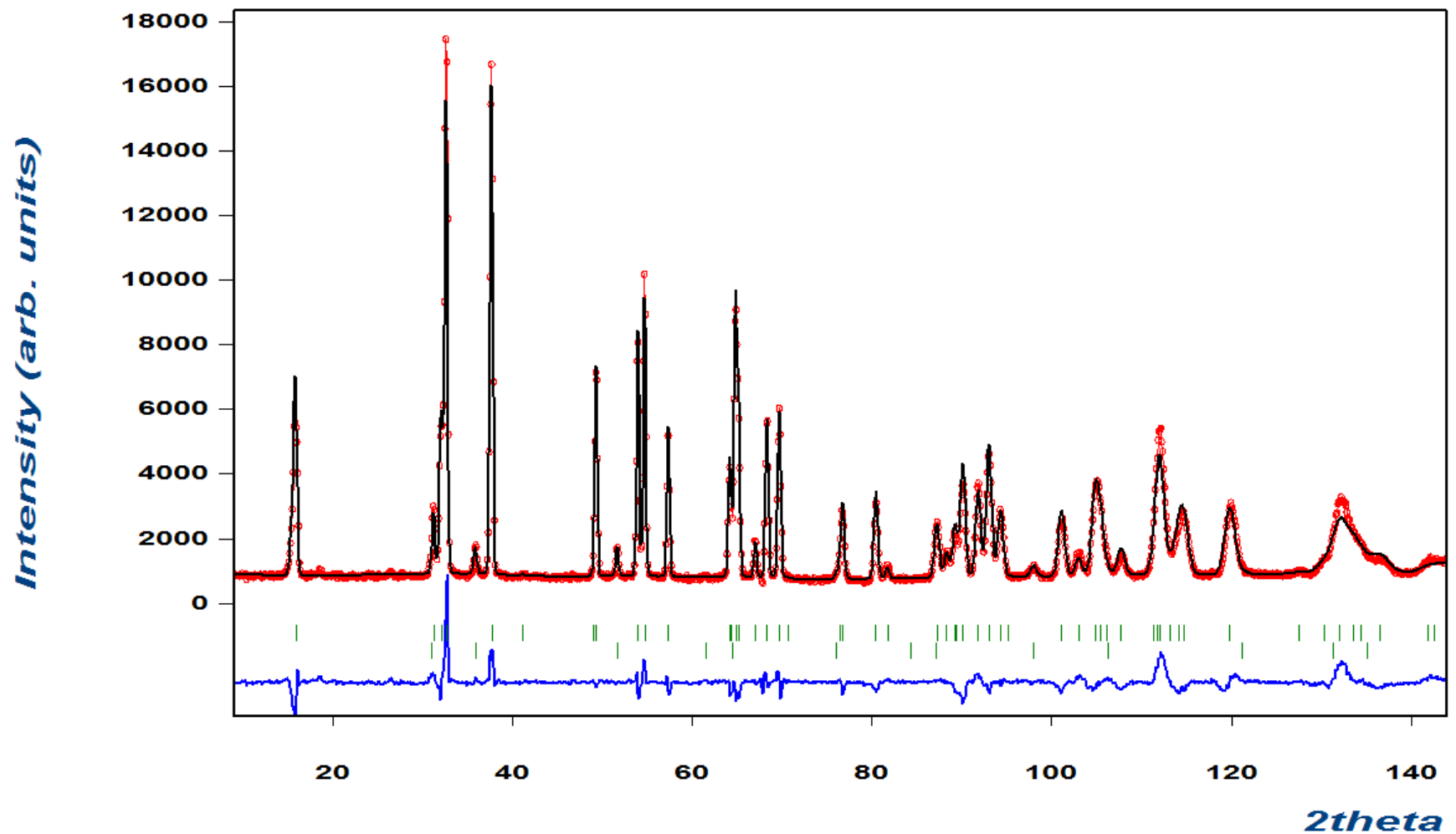
MgO

=> Bragg R-factor: 7.44%, R_f-factor= 4.70%

Vol: 99.033(0.004) Fract(%): 98.17(1.17)

Vol: 75.985(0.013) Fract(%): 1.83(0.12)

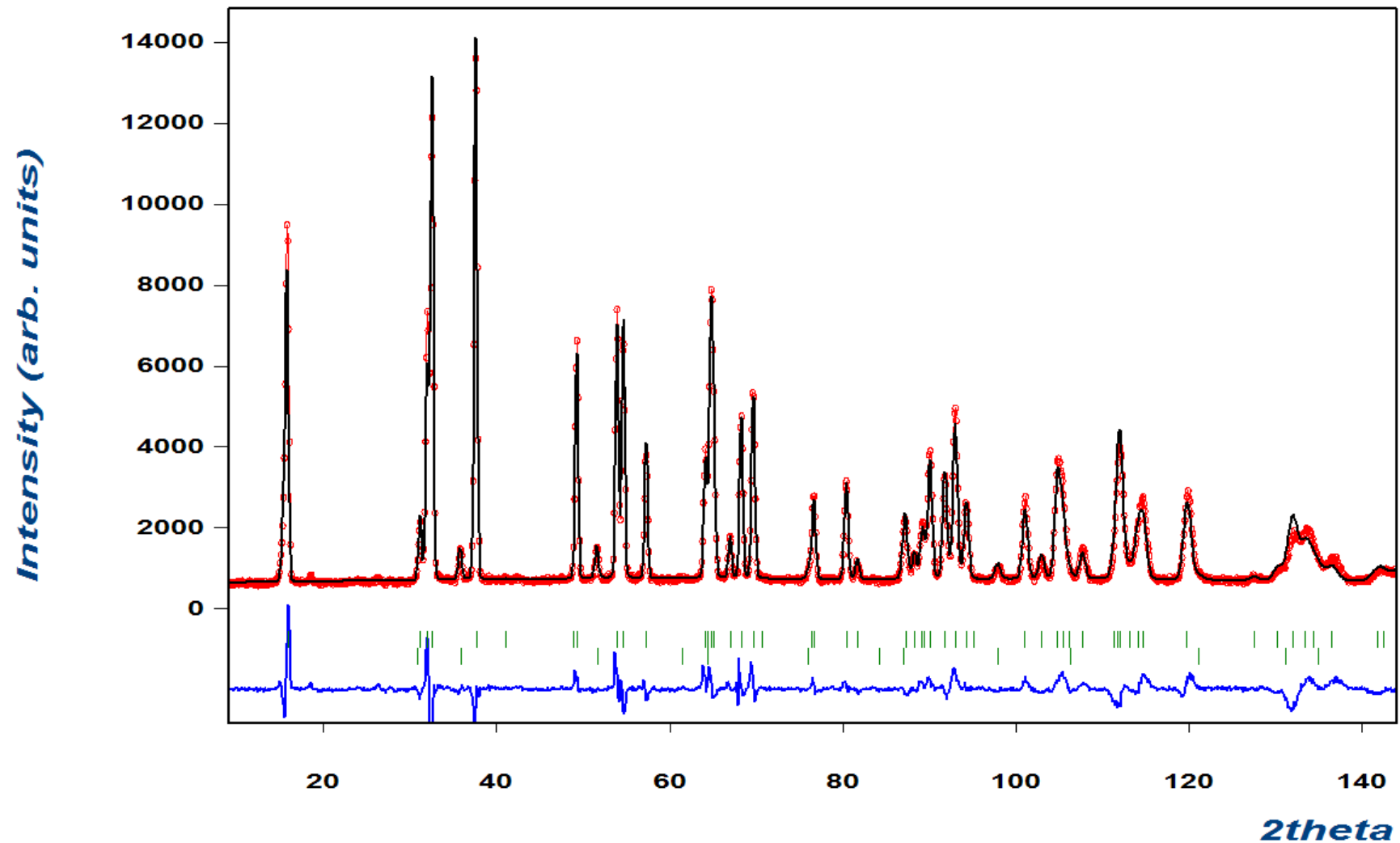
Cobaltite cathode material perpendicular to beam 1.3 Å 10' collimation 5/5



Ni-substrate
 => Bragg R-factor: 3.49%, Rf-factor= 1.55%
 NiO
 => Bragg R-factor: 5.79%, Rf-factor= 2.79%
 Rhombohedral cobaltite ($\text{LiMg}_x\text{Co}_{1-x}\text{O}_2$)
 => Bragg R-factor: 30.2%, Rf-factor= 16.6%

Vol: 44.049(0.003) Fract(%): 81.70(1.02)
 Vol: 72.635(0.000) Fract(%): 17.37(0.49)
 Vol: 99.033(0.000) Fract(%): 0.93(0.58)

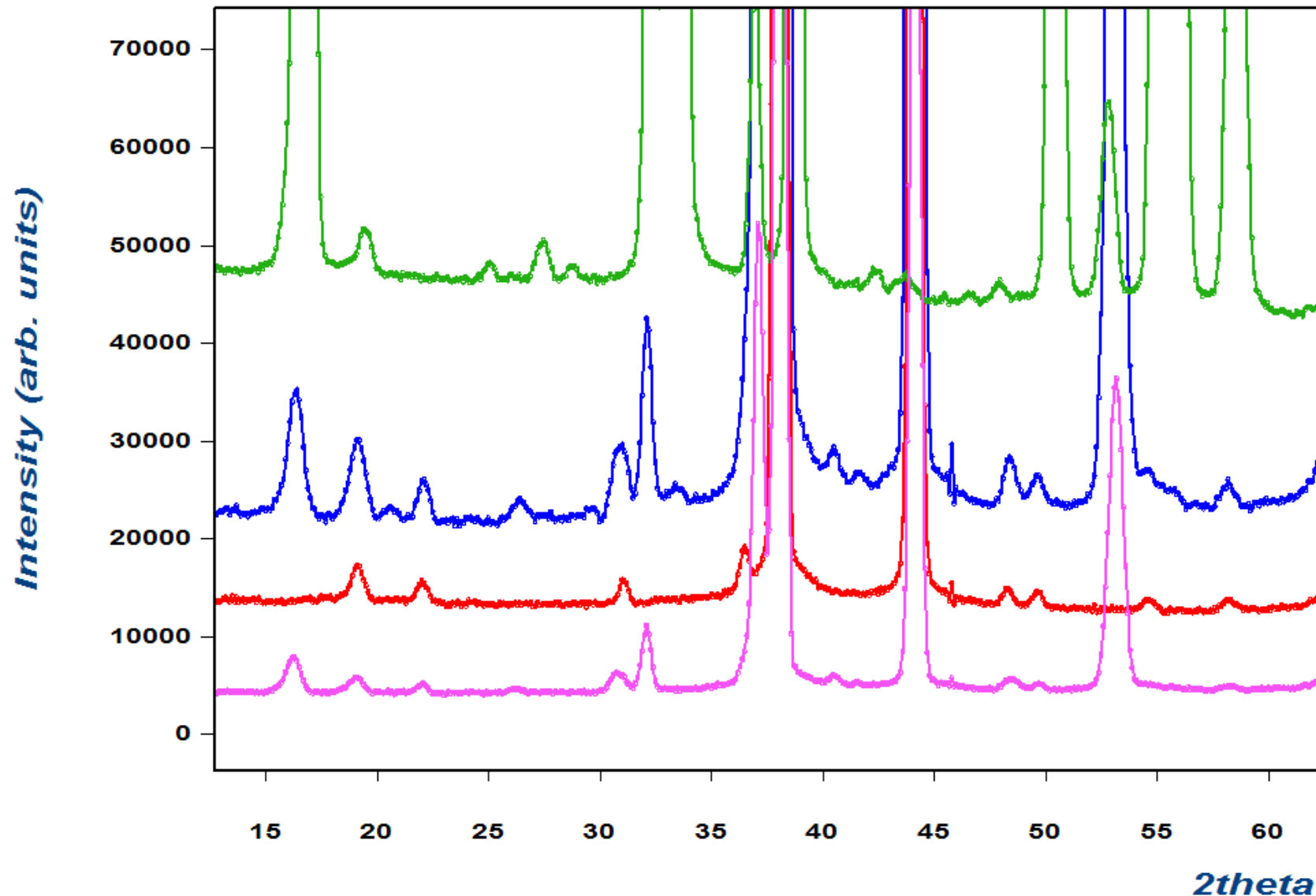
Cobaltite cathode material parallel to beam 1.3 Å 10' collimation 5/5 slit



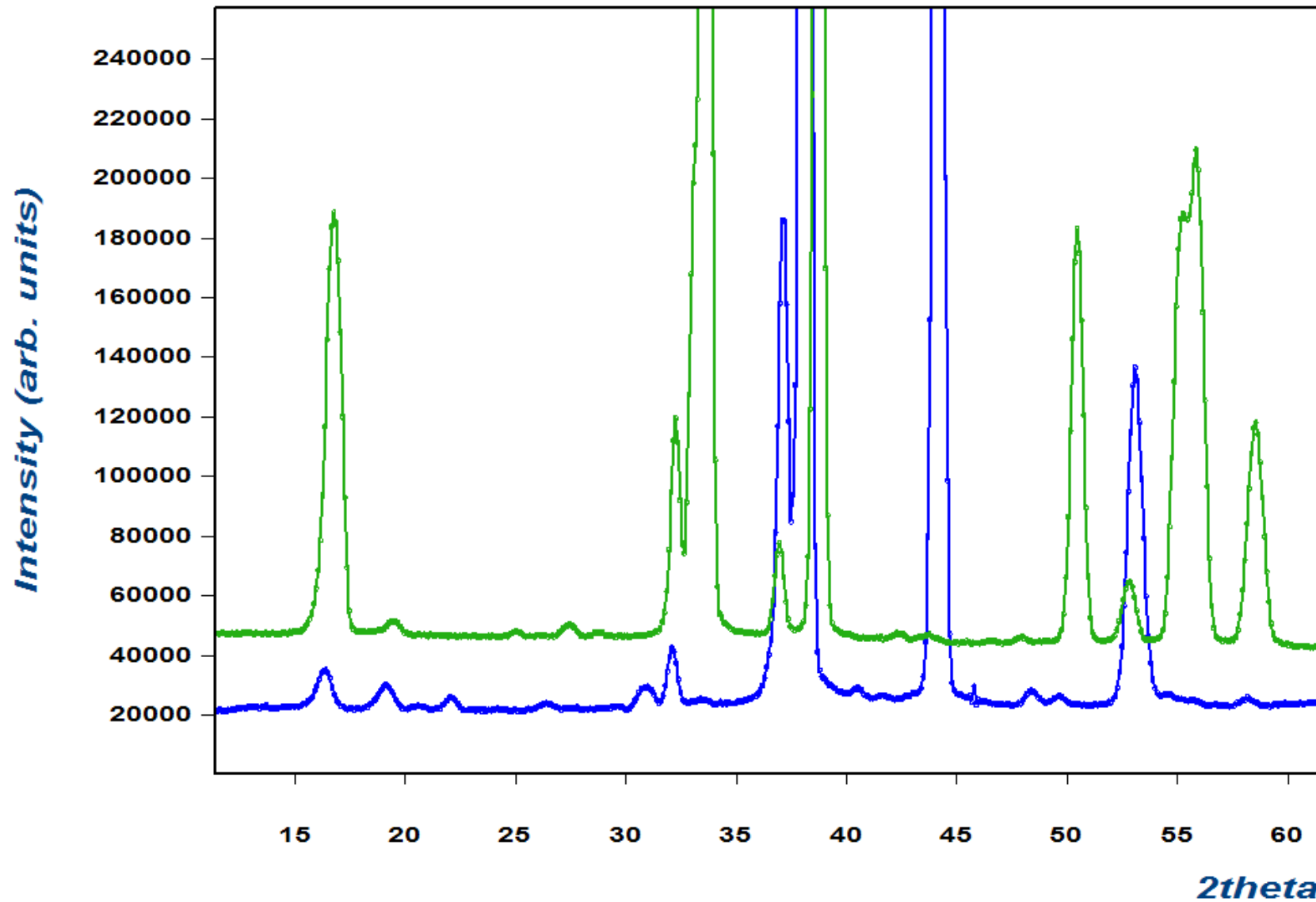
Details of the profile patterns of the as-received electrodes

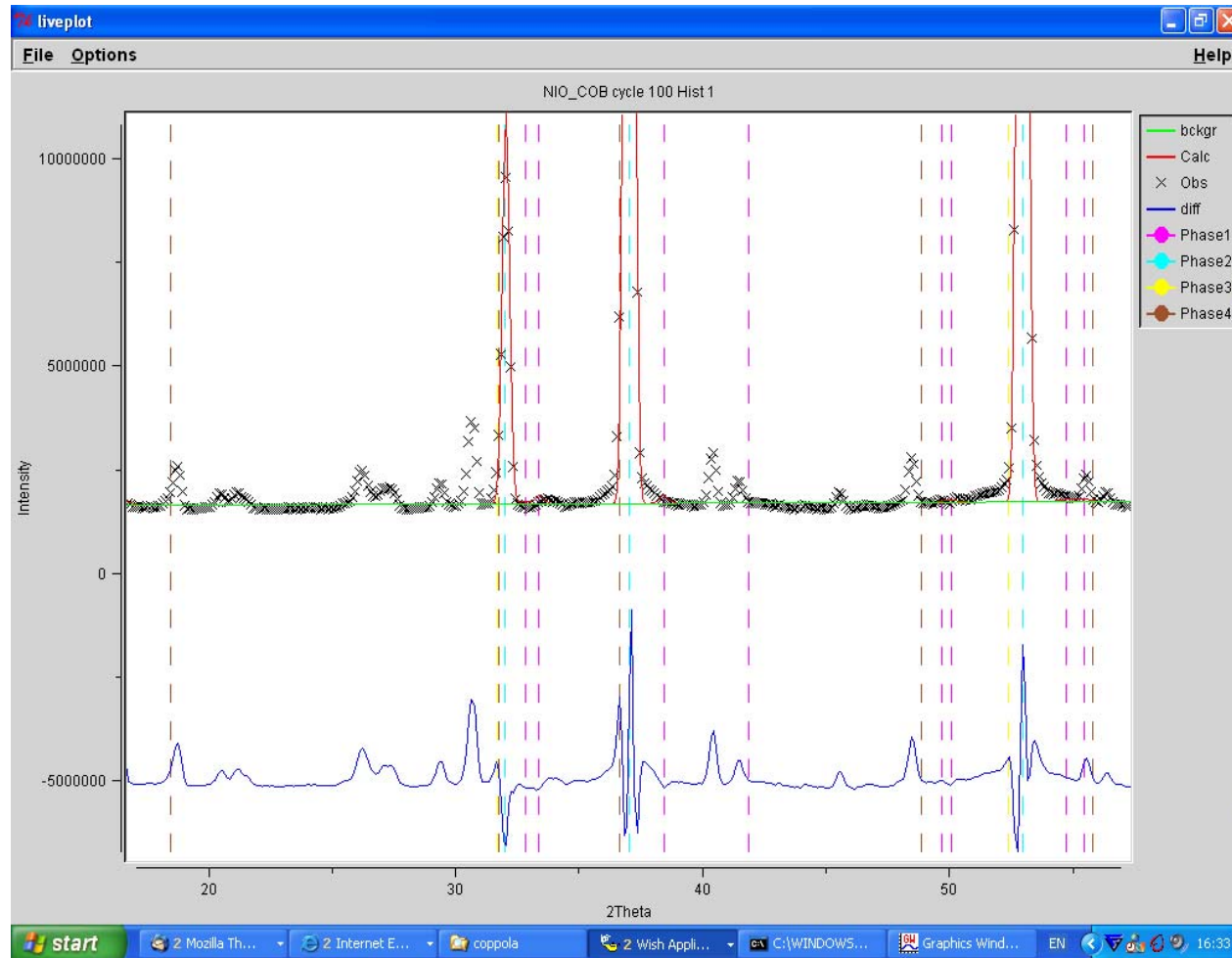
The patterns are: green - bulk cobaltite blue - deposited strips
 red - plain substrate pink - NiO/Ni substrate

The 2 main peaks for the bulk cobaltite are at 33.4deg and 38.8 deg 2theta. The 4 other strongest reflections (around 30-40% that of main peak) in the region of interest. It is the peak at 33.4deg that shows that the hexagonal phase is present on the deposited strips.



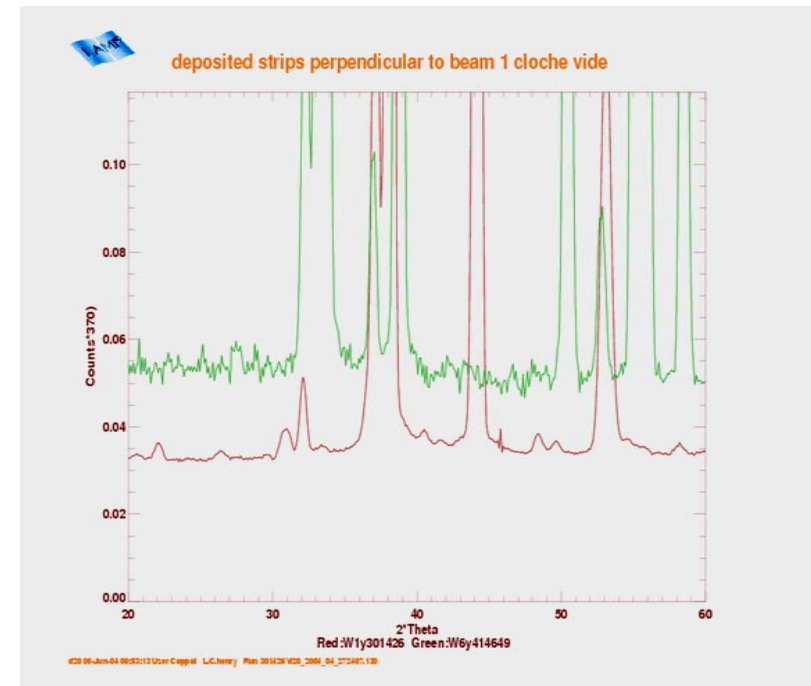
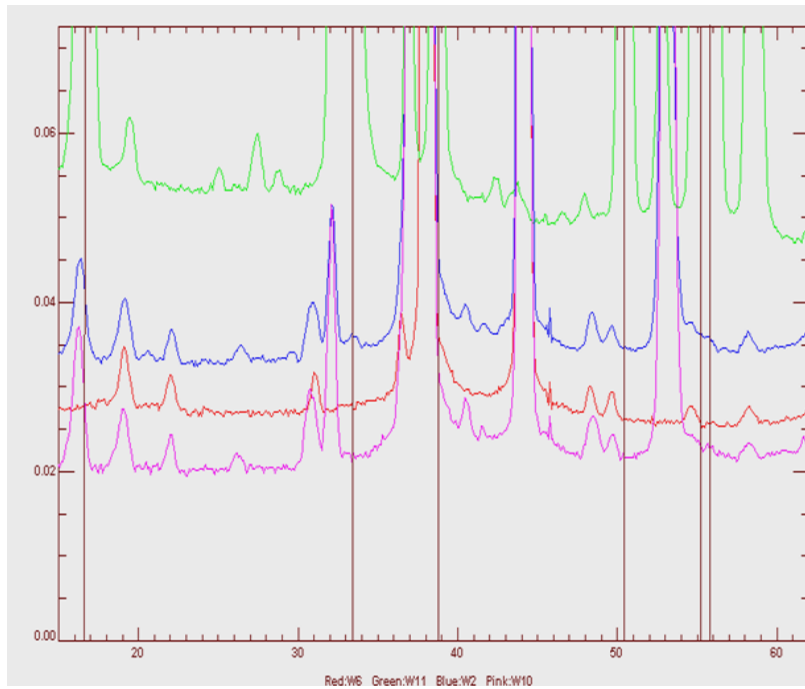
Bulk rhombohedral cobaltite (green) and deposited strips (blue). There are traces of R-cobaltite in the deposited strips





Profile patterns of the tested electrode Phase 1
 $\text{LiMg}_x\text{Co}_{1-x}\text{O}_2$
 Phase 2 NiO
 Phase 3 MgO
 Phase 4 Cobalt oxide

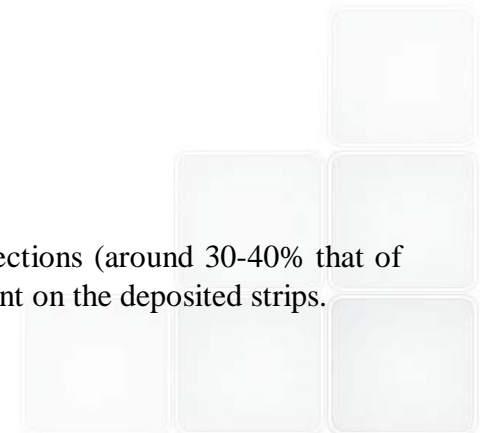




Profile patterns of the as-received electrode The patterns are:

- green - bulk cobaltite
- blue - deposited strips
- red - plain substrate
- pink - NiO/Ni substrate

The 2 main peaks for the bulk cobaltite are at 33.4deg and 38.8 deg 2theta. The 4 other strongest reflections (around 30-40% that of main peak) in the region of interest. It is the peak at 33.4deg that shows that the hexagonal phase is present on the deposited strips.



CONCLUSIONS

Ni/NiO-LiMg_{0.05}Co_{0.95}O₂ electrodes have been successfully investigated by neutron diffraction.

In the as-received electrode a cobaltite volume fraction of the order of 0.01 is estimated; after 100h at 650°C in the cell the initial crystallographic structure is completely changed but traces of hexagonal phase are still detectable.

The experimental conditions can be optimised by suppressing texture effects and increasing the cobaltite catalytic layer; high neutron flux is anyhow mandatory. Complementary EXAFS measurements should provide information on the phases present in the tested electrode and on its homogeneity.

References:

- E. Simonetti, R. Lo Presti, J. P. Sour. 160 (2006) 816
- R. Coppola, F. Bourée, L. Giorgi, Physica B 276 (2000) 862
- R. Coppola, P. F. Henry, A. Moreno, J. Rodriguez-Carvajal, E. Simonetti, Proc. MRS2010 Symp. W, San Francisco April 2010, J. of Ph. C.

