

*Dedicated to Professor Valer Fărcășan
at his 85th anniversary*

**SPINEL OXIDE COMPOSITE ELECTRODES.
II. PREPARATION, PHYSICO-CHEMICAL PROPERTIES AND
ELECTROCHEMICAL BEHAVIOUR OF CuCo_2O_4 AND
 $\text{Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ DEPOSITED ON Ni ELECTRODES**

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ABSTRACT. CuCo_2O_4 and $\text{Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ deposited on Ni electrodes (**Ni/CuCo₂O₄**, **Ni/Li_{0.1}Cu_{0.9}Co₂O₄**) were prepared by thermal decomposition of nitrate precursors deposited on Ni grating. The physico-chemical characterization showed that these oxides have a spinel structure. In the anodic potentials domain, cyclic voltammetry measurements performed on both **Ni/CuCo₂O₄** and **Ni/Li_{0.1}Cu_{0.9}Co₂O₄** electrodes showed the presence of the Co(IV/III) quasi-reversible redox transition, while in the cathodic potentials domain the Cu(II/I) transition was observed. The highest roughness factor (666) was obtained for **Ni/Li_{0.1}Cu_{0.9}Co₂O₄** electrode. The heterogeneous electron transfer rate constant values pointed out that the Co(IV/III) transition is faster on **Ni/Li_{0.1}Cu_{0.9}Co₂O₄** electrode.

Keywords: spinel oxide, copper-cobalt oxide, lithium-copper-cobalt oxide, composite electrodes.

INTRODUCTION

Cheap and easily prepared spinel-type oxides have been investigated extensively as electrodes for electrocatalytic processes, such as evolution and reduction of oxygen, as well as chlorine evolution [1, 2]. In these compounds, the cations of mixed valences favour the reversible adsorption of oxygen by providing donor-acceptor sites for its chemisorption [3]. Cobaltite binary oxides ($\text{M}_x\text{Co}_{3-x}\text{O}_4$ with $\text{M} = \text{Co}, \text{Ni}, \text{Mn}, \text{Cu}, \text{Zn}, \text{Li}$) have been obtained using various methods and conditions of preparation such as thermal decomposition [4-6], sol-gel synthesis [7] and cryochemical synthesis [8]. An effect of the nature of the substrate (Pt, Ni, Ti) was also put in evidence [9-11]. It was shown that the intercalation of Cu^{2+} into the Co_3O_4 matrix enhances the electrocatalytic activity of the spinel oxide [1]. Additionally, it has been demonstrated that Li-doping increased electrical conductivity and electrocatalytic properties of spinel oxides [11].

Continuing our preoccupations on the electrochemistry of composite electrodes [12, 13], in this paper **CuCo₂O₄ / Li_{0.1}Cu_{0.9}Co₂O₄** deposited on Ni grating electrodes were prepared by thermal decomposition of nitrate precursors deposited on a substrate of Ni grating. The morphological studies on the **Ni/CuCo₂O₄** and **Ni/Li_{0.1}Cu_{0.9}Co₂O₄** electrodes were done using scanning

electron microscopy (SEM). The surface composition was assessed through semiquantitative energy dispersive analysis of X-rays (EDAX), while the crystalline structure of the oxides was determined by X-ray diffraction. The electrochemical behaviour of the composite electrodes was studied by cyclic voltammetry, performed in 1 M NaOH solutions.

EXPERIMENTAL SECTION

Electrode preparation

CuCo₂O₄ / Li_{0.1}Cu_{0.9}Co₂O₄ deposited on Ni grating electrodes were prepared by thermal decomposition of nitrate precursors, deposited on a substrate of Ni grating. In this procedure, Cu(NO₃)₂·2.5 H₂O (*Fisher Scientific, ACS*) and Co(NO₃)₂·6H₂O (*Fisher Scientific, ACS*) were dissolved in the solvent mixture isopropanol : nanopure water (4 : 1), with the appropriate atomic ratio (Cu : Co) and concentration. The solution was deposited uniformly onto a Ni grating which had been previously degreased in dichloromethane (*Anachemia, ACS*) and thoroughly washed with nanopure water. The solvent was then evaporated at 100°C and the nitrate coating was heated for 15 min in a triple-zone quartz furnace (Lindberg 59744) under air atmosphere at 350°C. The procedure was repeated four times until the desired catalyst loading was achieved, and the electrodes were thereafter annealed over 1 h under the same conditions.

Morphology/structure investigation

Surface morphology of the oxide powders was examined with a scanning electron microscope (Hitachi, model S-2300) and the surface composition was assessed using an energy dispersive spectrometer.

X-ray diffraction patterns of the oxide powders were obtained using a Siemens model D5000 instrument with Co-K_α radiation (λ=1.789Å).

Electrochemical measurements

The cyclic voltammetry measurements were performed in a classical three-electrode electrochemical cell, containing: the working electrode (the composite electrode), the reference electrode (a saturated calomel electrode, SCE) and Pt as counter electrode (~1 cm²). The electrochemical cell was connected to a computer-controlled potentiostat (Autolab-PGSTAT10, Eco Chemie, Netherlands). The supporting electrolyte was a solution of 1 M NaOH (*Lachema, Czech Republic*).

RESULTS AND DISCUSSION

In order to estimate the degree of coverage of Ni grating electrodes with spinel oxides (**CuCo₂O₄**, **Li_{0.1}Cu_{0.9}Co₂O₄**), morphological studies on the prepared electrodes were carried out using a scanning electron microscopy (SEM) (Fig. 1). The surface composition was established through semiquantitative EDAX analysis.

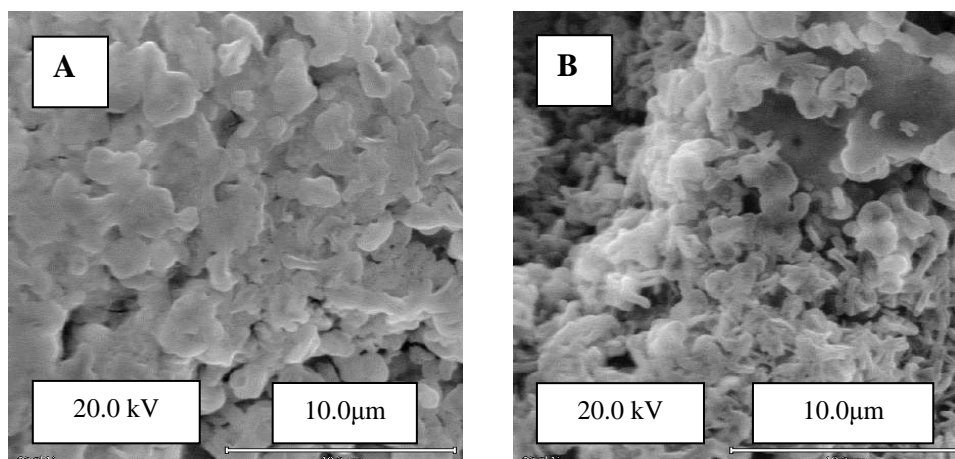


Fig. 1. SEM micrographs of $\text{Ni/CuCo}_2\text{O}_4$ (A) and $\text{Ni/Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ (B) electrodes, x5000.

The $\text{Ni/Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ electrode was more porous than $\text{Ni/CuCo}_2\text{O}_4$ electrode, which is in agreement with the observation made for the corresponding powders [13]. It is important to mention that Ni electrodes are completely covered by oxides for both investigated electrodes, assuring that only the oxide layer will dictate their electrochemical behaviour. EDAX analysis indicated the atomic ratio Cu : Co for $\text{Ni/CuCo}_2\text{O}_4$ of 0.51 and for $\text{Ni/Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ of 0.47, proving a composition very close to that corresponding to a stoichiometric ratio.

The X-ray diffraction analysis (Fig. 2) performed on $\text{Ni/CuCo}_2\text{O}_4$ and $\text{Ni/Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ electrodes pointed out the existence of a cubic spinel structure of the investigated oxides.

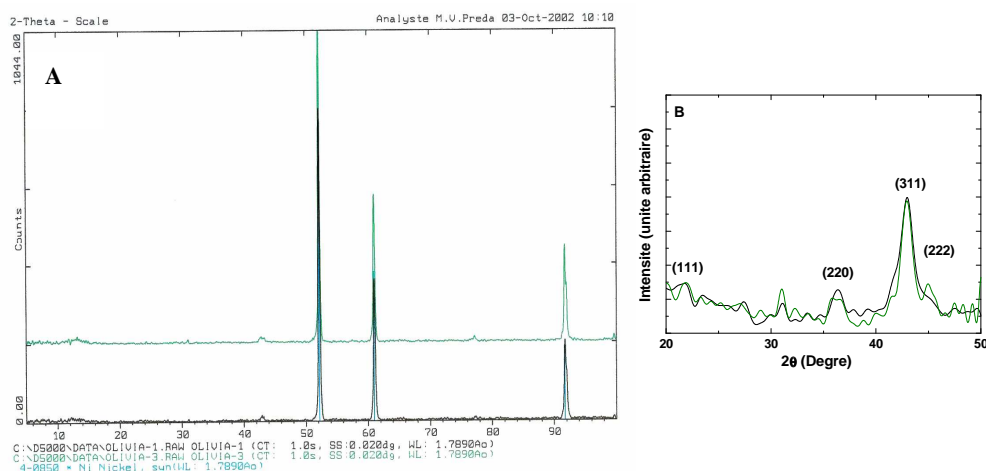


Fig. 2. X-ray diffractograms of $\text{Ni/CuCo}_2\text{O}_4$ (-) and $\text{Ni/Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ (-) electrodes.

The X-ray diffractograms (Fig. 2A) presents three well defined diffraction lines for Ni, at values of Bragg angles (2θ) of $\sim 52^\circ$, $\sim 61^\circ$ and $\sim 92^\circ$, due to the formation of a thin layer of spinel oxide on the Ni substrate. Diffractograms are limited to Bragg angles lying between 20° and 50° (Fig. 2B) because of the high intensity of the diffraction lines of the nickel substrate in comparison to those of the oxide phase in the region 50° - 90° . The positions of the diffraction lines and their relative intensity in the copper-cobalt oxide powder were in good agreement with data for $\text{Cu}_{0.92}\text{Co}_{2.08}\text{O}_4$ [14].

The electrochemical behavior for **Ni/CuCo₂O₄** and **Ni/Li_{0.1}Cu_{0.9}Co₂O₄** electrodes was investigated by cyclic voltammetry measurements at different scan rates (Fig. 3).

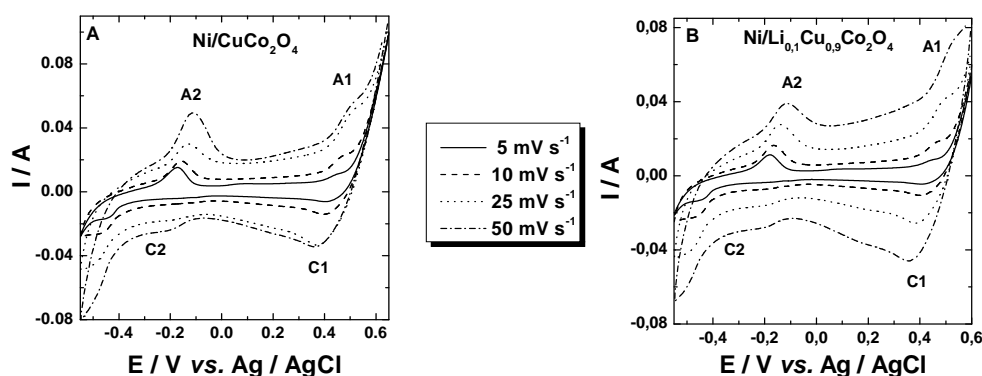
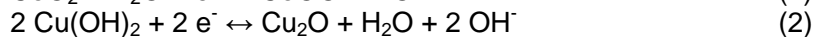
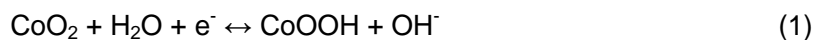


Fig. 3. Influence of potential scan rate on the electrochemical behaviour of **Ni/CuCo₂O₄** (A) and **Ni/Li_{0.1}Cu_{0.9}Co₂O₄** (B) electrodes. Experimental conditions: starting potential, 0.65 V vs. Ag/AgCl (A), 0.6 V vs. Ag/AgCl (B); supporting electrolyte, 1 M NaOH.

The cyclic voltammograms of **Ni/CuCo₂O₄** and **Ni/Li_{0.1}Cu_{0.9}Co₂O₄** (Fig. 3) showed in the positive potential region the presence of the redox quasi-reversible transitions Co(IV/III) (A1/C1, equation 1) [15] and in the negative potential region, the transitions Cu(II/I) (A2/C2, equation 2) [16]:



The roughness factor (R_F), defined as the ratio of the real surface area to the geometric area of a rugous film, was measured as the ratio between the double-layer capacitance for the investigated oxide/electrolyte interface (C_{dl}) and the double-layer capacitance for an ideally smooth oxide surface $60 \mu\text{F cm}^{-2}$ [17]. The double-layer capacitance for the investigated oxide/electrolyte interface was estimated using cyclic voltammograms recorded at different scan rates in the capacitive region, by assuming no adsorption pseudo-capacitance. C_{dl} was calculated from the slope of the linear curve I_{cap} vs. scan rate (Fig. 4) [9]:

$$C_{dl} = \frac{di_{cap}}{d\left(\frac{\delta E}{\delta t}\right)} \quad (3)$$

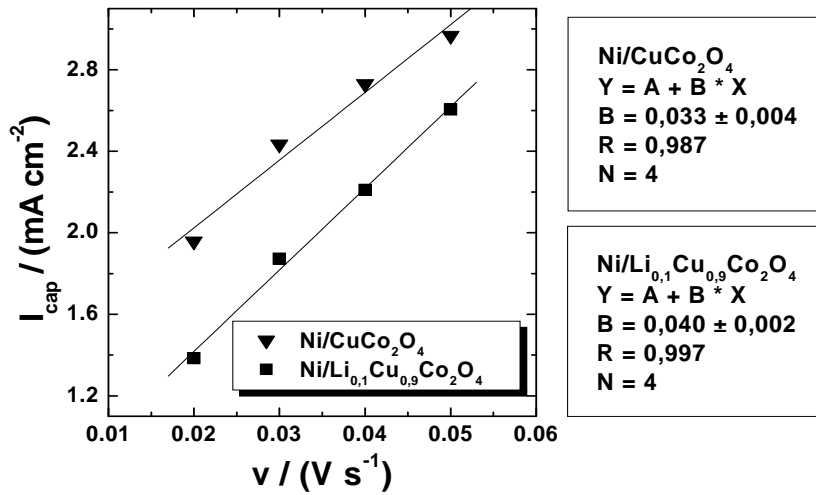


Fig. 4. Dependence of the capacitive current on the potential scan rate in the region corresponding to double-layer charging.

The R_F value for **Ni/CuCo₂O₄** was found to be 550, while for **Ni/Li_{0,1}Cu_{0,9}Co₂O₄** was of 666. The results are in agreement with those presented in the literature, showing that the R_F for Li containing oxides is higher than for the copper-cobalt oxides, and are in agreement with SEM measurements, too [18].

The values of the heterogeneous electron transfer rate constant (k_s) were estimated for **Ni/CuCo₂O₄** and for **Ni/Li_{0,1}Cu_{0,9}Co₂O₄** electrodes using Laviron's method for potential peak split $\Delta E_p < \frac{200}{n}$ (mV) where, n represents the number of electrons, and all other parameters have the common meaning, and considering $\alpha \approx 0.5$ [19]. Thus, using the calculated values [18] the dependence $n\Delta E_p$ vs. m^{-1} was plotted (Fig. 5), where n stands for the number of electrons and m is a parameter defined by the relation:

$$m = \frac{k_s}{nv} \cdot \frac{RT}{F} \quad (4)$$

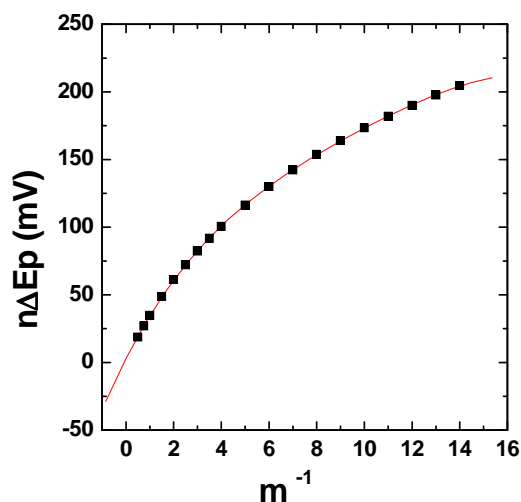


Fig. 5. Variation of $n\Delta E_p$ with m^{-1} [18].

Using the plot from Fig. 5 the m values corresponding to the experimental values of $n\Delta E_p$, measured for different potential scan rates for **Ni/CuCo₂O₄** and **Ni/Li_{0.1}Cu_{0.9}Co₂O₄** electrodes, were estimated. Then, from the relation (4) the k_s values at different potential scan rates were calculated (Table 1).

The k_s values point out that the Co(IV/III) transition is faster on **Ni/Li_{0.1}Cu_{0.9}Co₂O₄** electrode than on **Ni/CuCo₂O₄** electrode. In all cases, the values of the rate constants for the heterogeneous electron transfer indicate that the corresponding electrode processes can be considered as quasi-reversible ones.

Table 1.

Heterogeneous electron transfer rate constant (k_s) values corresponding to the Co(IV/III) transition for **Ni/CuCo₂O₄** and **Ni/Li_{0.1}Cu_{0.9}Co₂O₄** electrodes.

ν (mV s ⁻¹)	ΔE_p (mV)	m	k_s (s ⁻¹)
Ni/CuCo₂O₄			
5	43	0.78	0.15
10	75	0.37	0.15
25	144	0.14	0.14
			$\bar{k}_s = 0.15$
Ni/Li_{0.1}Cu_{0.9}Co₂O₄			
10	55	0.57	0.22
25	105	0.23	0.23
50	161	0.11	0.22
			$\bar{k}_s = 0.22$

CONCLUSIONS

The preparation, the morphological and structural characterization, as well as the investigation of the electrochemical behavior of Ni electrodes covered by spinel oxides (CuCo_2O_4 , $\text{Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$) conducted to the following conclusions:

- The SEM micrographs show that $\text{Ni/Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ electrode is more porous than $\text{Ni/CuCo}_2\text{O}_4$ electrode, which is in agreement with the observation made for the corresponding oxides powders.
- The analysis of $\text{Ni/CuCo}_2\text{O}_4$ and $\text{Ni/Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ electrodes by X-ray diffraction proved the existence of a cubic spinel structure.
- The roughness factor for $\text{Ni/Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ is higher than for $\text{Ni/CuCo}_2\text{O}_4$ which is in agreement with SEM measurements.
- For both investigated electrodes $\text{Ni/CuCo}_2\text{O}_4$ and $\text{Ni/Li}_{0.1}\text{Cu}_{0.9}\text{Co}_2\text{O}_4$ the voltametric response indicates the presence of redox cuasi-reversible transitions Co(IV/III) and Cu(II/I) .

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