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Dedicated to Professor Valer Fărcăşan at his 85th anniversary

SPINEL OXIDE COMPOSITE ELECTRODES. I. $CuCo_2O_4$ AND $Li_{0.1}Cu_{0.9}Co_2O_4$ CARBON PASTE ELECTRODES FOR H_2O_2 OXIDATION/REDUCTION

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ABSTRACT. A new method to obtain composite electrodes based on **$CuCo_2O_4$** and **$Li_{0.1}Cu_{0.9}Co_2O_4$** spinel-type oxides, is presented. Both oxides were prepared as powders by thermal decomposition of nitrate precursors. In the anodic potentials domain, cyclic voltammetry measurements performed on **$CuCo_2O_4$**-carbon paste electrodes (**CPEs**) showed the presence of Co(IV/III) and Co(III/II) quasi-reversible redox transitions, while in the cathodic potentials domain Cu(II/I) and Cu(I/0) transitions were observed. Contrarily, at **$Li_{0.1}Cu_{0.9}Co_2O_4$-CPEs,** only Co(III/II) transition was noticed. The electrochemical response of both electrodes, recorded in the presence of H_2O_2, proved a moderate electrocatalytic activity toward H_2O_2 oxidation/reduction.

Keywords: copper-cobalt oxide, **$Li_{0.1}Cu_{0.9}Co_2O_4$** oxide, carbon paste electrode, H_2O_2 oxidation/reduction.

INTRODUCTION

Transition metal oxides, especially spinel-type oxides, represent versatile materials for electrocatalysis [1,2]. Studies on the physico-chemical and electrochemical catalytic properties of complex oxides with spinel structure have received considerable attention during recent years [3-7], as they are low-cost, easily available, reasonably stable and catalytically active materials.

Among spinel-type oxides, copper-cobalt spinels are of interest for CO oxidation in the presence of O_2 as well as for the conversion of synthesis gas ($CO/CO_2/H_2$) to higher alcohols [8]. $CuCo_2O_4$ and $NiCo_2O_4$ are highly effective in removing CO, NO and hydrocarbons from waste and exhaust gases in the absence of oxygen at 350ºC [1]. $CuCo_2O_4$ has a high catalytic activity for xylene complete oxidation [9]. It was shown that the intercalation of Cu^{2+} into the Co_3O_4 matrix enhances the electrocatalytic activity of the spinel oxide for anodic oxygen evolution [8]. Additionally, it has been demonstrated that Li-doping increases the electrical conductivity and electrocatalytic properties of spinel oxides [5]. Their electrochemical characterization has been carried out especially on thin films obtained on suitable substrates (either conducting or non-conducting) [10-13].

Spinel oxides powders have been obtained using various methods of preparation such as (i) thermal decomposition of mixed nitrates, carbonates or hydroxides [3, 14, 15]; (ii) sol-gel method [16]; and (iii) freeze drying method [17]. Spinel oxides thin films have been prepared by chemical spray pyrolysis [18] or by cathodic sputtering [19].

Continuing our preoccupations in the domain of spinel oxides-modified electrodes [20], in this paper a new method to obtain composite electrodes based on powders of spinel-type oxides is presented. The method exploits the major advantages of carbon paste electrodes, which consist in using small amounts of substances, renewability, exceptionally low background currents, a wide operating potential window, a convenient modification, miniaturization and low-cost [21]. The composite electrodes were obtained by hand-mixing $\mathbf{CuCo_2O_4}$ or $\mathbf{Li_{0.1}Cu_{0.9}Co_2O_4}$ with graphite powder and paraffin oil. The investigated oxides were prepared as powders by thermal decomposition of nitrate precursors. The morphological studies on the obtained spinel oxides powders 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. The electrocatalytic response in the presence of H_2O_2 was also investigated.

EXPERIMENTAL SECTION

Materials

The $\mathbf{CuCo_2O_4}$ and $\mathbf{Li_{0.1}Cu_{0.9}Co_2O_4}$ oxides were obtained as powders by evaporating the aqueous solutions of the corresponding metals nitrates, $Cu(NO_3)_2 \cdot 2.5\ H_2O$ (*Fisher Scientific, ACS*) and $Co(NO_3)_2 \cdot 6H_2O$ (*Fisher Scientific, ACS*), followed by the thermal decomposition of the obtained mixtures at 350^{o}C, in a triple-zone quartz furnace (Lindberg 59744) under air atmosphere.

Graphite powder and paraffin oil were purchased from *Fluka* and used as received. The supporting electrolyte was a solution of 1 M NaOH (*Lachema, Czech Republic*).

Electrode preparation

The carbon paste electrodes (**CPEs**) modified with $\mathbf{CuCo_2O_4}$ (**$\mathbf{CuCo_2O_4}$-CPE**) or $\mathbf{Li_{0.1}Cu_{0.9}Co_2O_4}$ (**$\mathbf{Li_{0.1}Cu_{0.9}Co_2O_4}$-CPE**) were prepared by mixing 50 mg of graphite powder and 50 mg of oxide powder with 40 μL of paraffin oil.

A portion of the resulting paste was packed firmly into the cavity of a Teflon tube electrode (3 mm diameter). The electric contact was established *via* a copper wire. The surface of the resulting carbon paste electrode was manually smoothed on a clean paper.

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 wire as counter-electrode (~1 cm^2). The electrochemical cell was connected to a computer-controlled potentiostat (Autolab-PGSTAT10, Eco Chemie, Netherlands).

RESULTS AND DISCUSSION

In order to estimate the dimensions of the oxide particles, morphological studies on the prepared spinel oxides powders (**$CuCo_2O_4$**, **$Li_{0.1}Cu_{0.9}Co_2O_4$**) were carried out using scanning electron microscopy (SEM). The surface composition was established through semiquantitative EDAX analysis.

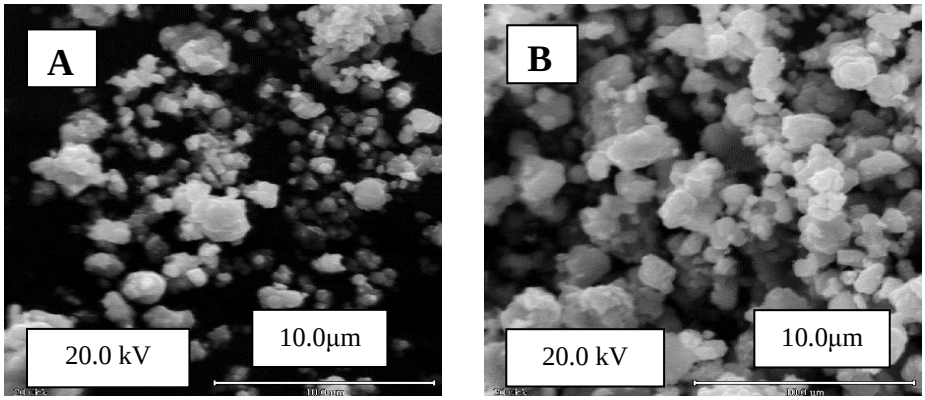

Fig. 1. SEM micrographs of **$CuCo_2O_4$** (A) and **$Li_{0.1}Cu_{0.9}Co_2O_4$** (B) powders (x5000)**.**

The **$Li_{0.1}Cu_{0.9}Co_2O_4$** powder (Fig. 1) was more porous and more uniform than **$CuCo_2O_4$** powder. EDAX analysis indicated a Cu:Co atomic ratio of 0.51 for **$CuCo_2O_4$** and of 0.46 for **$Li_{0.1}Cu_{0.9}Co_2O_4$**, proving a composition very close to that corresponding to the expected stoichiometric ratio.

The X-ray diffraction analysis (Fig. 2) performed on the oxides powders (**$CuCo_2O_4$**, **$Li_{0.1}Cu_{0.9}Co_2O_4$**) pointed out to the existence of a face-centered cubic spinel structure.

The positions of the diffraction lines and their relative intensity for the copper-cobalt oxide powder are in good agreement with data for $Cu_{0.95}Co_{2.05}O_4$ [22]. A partial substitution (10%) of copper with lithium led to an increase of t he peaks diffraction intensity, indicating an increase of the oxide cristallinity. In the same time, the diffraction peaks for **$Li_{0.1}Cu_{0.9}Co_2O_4$** oxide were slightly shifted toward higher values of Bragg angles, showing a decrease of the lattice parameter.

The voltammetric responses of the carbon paste electrodes incorporating the two spinel oxides, **$CuCo_2O_4$** and **$Li_{0.1}Cu_{0.9}Co_2O_4$**, usually considered as an electrochemical "fingerprint" of the electroactive compound, are presented in Fig. 3.

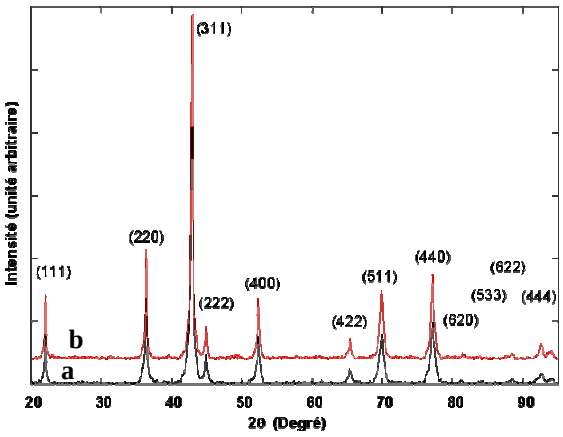

Fig. 2. X-ray diffractograms of **$CuCo_2O_4$** (a) and **$Li_{0.1}Cu_{0.9}Co_2O_4$** (b) powders.

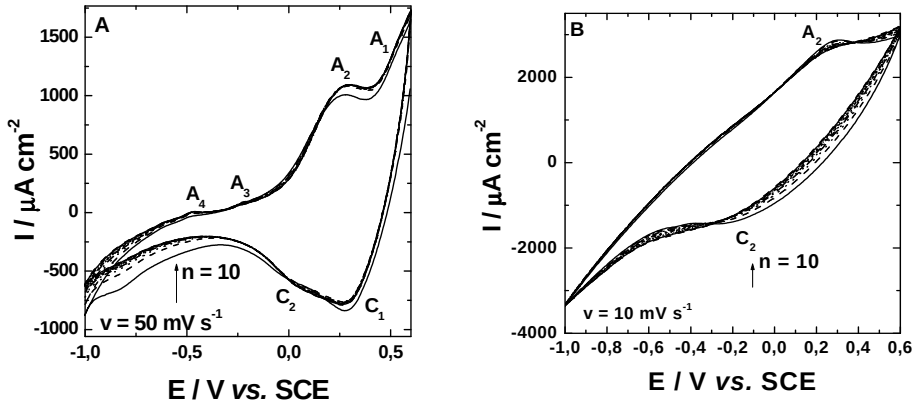

Fig. 3. Repetitive cyclic voltammograms recorded at **$CuCo_2O_4$-CPE** (A) and **$Li_{0.1}Cu_{0.9}Co_2O_4$-CPE** (B). Experimental conditions: supporting electrolyte, 1 M NaOH; starting potential, +0.6 V *vs.* SCE; n-cycle number.

A minor variation of the current intensity observed during repetitive potential cycling in the potential domain where the investigated oxide is electrochemically active, proved the stability of the studied electrodes.

In the positive potentials region, the voltammetric response of **$CuCo_2O_4$-CPE** showed the presence of two quasi-reversible redox transitions (A_1/C_1 and A_2/C_2, see Fig. 3A). The first transition was attributed to the Co(IV/III) couple, involved in the following process [23]:

$CoO_2 + H_2O + e^- \Leftrightarrow CoOOH + OH^-$ (A_1/C_1)

The second transition was attributed to the Co(III/II) redox couple:

$CoOOH + H_2O + e^- \Leftrightarrow Co(OH)_2 + OH^-$ (A_2/C_2)

In the negative potentials region, the voltammetric response of **$CuCo_2O_4$-CPE** showed the presence of two redox transitions (A_3 and A_4 from Fig. 3A). The first transition was attributed to Cu(II/I) redox couple [24]:

$2\ Cu(OH)_2 + 2\ e^- \Leftarrow Cu_2O + H_2O + 2\ OH^-$ (A_3)

The second transition was attributed to Cu(I/0) [24]:

$Cu_2O + H_2O + 2\ e^- \Leftarrow 2\ Cu + 2\ OH^-$ (A_4)

The cyclic voltammogram recorded at **$Li_{0.1}Cu_{0.9}Co_2O_4$-CPE** (Fig. 3B) presented only one peak pair (A_2/C_2) corresponding to the Co(III/II) redox transition.

The voltammetric responses recorded in the presence of H_2O_2 for both **$CuCo_2O_4$-CPE** and **$Li_{0.1}Cu_{0.9}Co_2O_4$-CPE** are presented in Fig. 4.

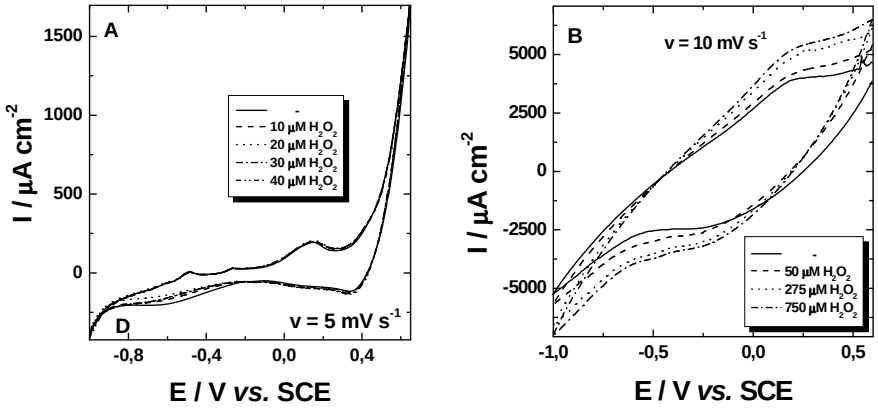

Fig. 4. Cyclic voltammograms recorded at **$CuCo_2O_4$– CPE** (A) and **$Li_{0.1}Cu_{0.9}Co_2O_4$-CPE** (B) in the absence and in the presence of H_2O_2. Experimental conditions: supporting electrolyte, 1 M NaOH; starting potential, +0.65 V *vs.* SCE (A) and +0.6 V *vs.* SCE (B).

The addition of 40 µM H_2O_2 in the electrolyte solution does not change significantly the cyclic voltammograms of **$CuCo_2O_4$-CPE** (Fig. 4A), while the addition of almost the same concentration of H_2O_2 (50 µM) induced an important increase of both oxidation and reduction peak currents for **$Li_{0.1}Cu_{0.9}Co_2O_4$-CPE** (Fig. 4B). Additionally, for this electrode, further increases of peak currents with the increase of H_2O_2 concentration were observed. These results indicate that **$Li_{0.1}Cu_{0.9}Co_2O_4$-CPE** has a moderate electrocatalytic activity toward H_2O_2 oxidation/reduction, described by the following reactions:

$HO_2^- + OH^- \rightarrow O_2 + H_2O + 2\ e^-$ (1)

$HO_2^- + H_2O + 2\ e^- \rightarrow 3\ OH^-$ (2)

CONCLUSIONS

The physico-chemical and electrochemical characterization of **$CuCo_2O_4$-CPE** and **$Li_{0.1}Cu_{0.9}Co_2O_4$-CPE** led to the following conclusions:

- The SEM micrographs showed that **$Li_{0.1}Cu_{0.9}Co_2O_4$** powder is more porous than **$CuCo_2O_4$** powder.
- The analysis of the investigated oxide powders by X-ray diffraction proved the existence of a face-centered cubic spinel structure.
- Cyclic voltammetry measurements performed at **$CuCo_2O_4$-CPEs** indicated the presence of the quasi-reversible redox transitions Co(IV/III) and Co(III/II) in the anodic potentials domain, and the transitions Cu(II/I) and Cu(I/0) in the cathodic potentials domain. For **$Li_{0.1}Cu_{0.9}Co_2O_4$-CPE**, only one peak pair due to the Co(III/II) redox transition was observed.
- **$Li_{0.1}Cu_{0.9}Co_2O_4$-CPE** presented a better electrocatalytic activity toward H_2O_2 oxidation/reduction than **$CuCo_2O_4$-CPE**.

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