

## XPS Characterization of $\text{Li}_x\text{Cu}_{1-x}\text{Co}_2\text{O}_4$ Electrodes for the Oxygen Evolution Reaction

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### INTRODUCTION

Much interest has been centred in recent years on the development of highly catalytic materials for the oxygen evolution reaction (OER), since it participates as co-reaction in a large number of industrial processes such as electrolytic hydrogen production, recharge of metal-air batteries and metal electrowinning. Spinel-type oxides, particularly cobaltites with the general formula  $\text{MCo}_2\text{O}_4$ , where M represents a transition metal such as Co, Ni, Mn or Cu, are considered as candidates for replacing dimensionally stable anodes (DSA) which are expensive and unstable in concentrated alkaline solutions. Copper-cobalt oxide,  $\text{Cu}_y\text{Co}_{3-y}\text{O}_4$  ( $y \sim 1$ ), which is among the highest active anode materials for the OER in alkaline medium besides spinel  $\text{NiCo}_2\text{O}_4$  and perovskite  $\text{LaNiO}_3$ , is nonstoichiometric and exhibits p-type semiconducting properties (1). In order to increase the intrinsic electrocatalytic activity of the mixed copper-cobalt oxide, we carried out a partial substitution (0-40%) of Cu by Li in the spinel lattice. Indeed,  $\text{Li}_x\text{Cu}_{1-x}\text{Co}_2\text{O}_4$  ( $0 \leq x \leq 0.4$ ) powders have been recently synthesized by thermal decomposition of the nitrate precursors in the temperature range 300-500°C, and characterized using various techniques (2). It was shown that all the oxides crystallize in a monophasic face-centered cubic spinel structure (solid solution) that begins to decompose at 500°C with formation of CuO and  $\text{Co}_3\text{O}_4$ , and that the crystal lattice parameter decreases as the preparation temperature and Li content are increased. Substitution of Co by Cu is believed to take place predominantly in octahedral sites and the introduction of  $\text{Li}^+$  would generate  $\text{Co}^{3+}$  and  $\text{Cu}^{3+}$  ions, also in the octahedral sites of the spinel structure.

In order to support this conclusion, the present work aims at carrying out X-ray photoelectron spectroscopy (XPS) measurements on Li-doped oxide films of the same compositions ( $0 \leq x \leq 0.4$ ), prepared at 350°C on a nickel substrate using the chemical spray pyrolysis method.

### EXPERIMENTAL

$\text{Li}_x\text{Cu}_{1-x}\text{Co}_2\text{O}_4$  ( $0 \leq x \leq 0.4$ ) electrodes were prepared by chemical spray pyrolysis of an aqueous solution of lithium ( $x$  M), copper ( $0.01-x$  M) and cobalt (0.02 M) nitrates, on a clean polished nickel disk support (99.5%, 12.7 mm dia., 1 mm thick) heated at 330°C. The thin films were then annealed for 1 h at 350°C. The chemical spray pyrolysis apparatus and method have been described in a previous work (1). The spray is made using a brass nozzle in which compressed air passes at a pressure of 5 Psi. The nitrate solution is directed toward the nozzle with a syringe pump (Sage Instruments, model 355) set at a flow rate of  $0.5 \text{ mL min}^{-1}$  (3s) and then  $0.05 \text{ mL min}^{-1}$  ( $\sim 10$  min) until a  $2.5 \text{ mg cm}^{-2}$  oxide loading had been reached.

XPS measurements, carried out on as-prepared and

polarized electrodes, were performed in a Escalab 220iXL (V.G. Scientific) apparatus using  $\text{Al-K}\alpha$  radiation (1486.6 eV). The C1s line (284.8 eV) of the carbonates and/or hydrocarbons impurities detected at the sample surface was used as an internal standard. The XPS spectra resolution was  $\sim 0.5$  eV and peaks deconvolution was made using Origin v.5 software (Data Analysis and Technical Graphics, Microcal Software).  $\text{Li}_x\text{Cu}_{1-x}\text{Co}_2\text{O}_4$  electrodes (exposed area:  $0.95 \text{ cm}^2$ ) were polarized for 1h at a current density of  $780 \text{ mA cm}^{-2}$  in a Teflon electrochemical cell containing 1 M KOH (25°C), a  $7 \text{ cm}^2$  Pt disk (0.1 mm thick) auxiliary electrode and a Hg/HgO reference electrode; the cell has been described in detail elsewhere (1). Polarization was carried out using a Solartron 1287 electrochemical interface.

### RESULTS AND DISCUSSION

Binding energies (BE) of the Cu2p, Co2p and O1s transitions of as-prepared  $\text{Li}_x\text{Cu}_{1-x}\text{Co}_2\text{O}_4/\text{Ni}$  electrodes seem to be independent of the Li content ( $x$  value). However, peak  $\text{O}_1$ , attributed to stoichiometric oxygen  $\text{O}^{2-}$ , shows lower BE relative to that of pure  $\text{Co}_3\text{O}_4$ . Chemical shift of oxygen  $\text{O}_1$  is consistent with the absence of a  $\text{Co}_3\text{O}_4$  spinel phase at the surface of Li-doped copper-cobalt oxide electrodes, as reported previously (2), and with the formation of thin film  $\text{Li}_x\text{Cu}_{1-x}\text{Co}_2\text{O}_4$  solid solutions on nickel.

Quantitative analyses have shown, as expected, that total cobalt concentration is independent of the Li content. However, total copper concentration, that should decrease with an increase of Li doping, is increasing from the 30% Li composition, indicating an enrichment of copper at the surface of these electrodes. This phenomenon is explained by the tendency of  $\text{Cu}^{2+}$  ions to undergo a Jahn-Teller effect. After polarization, the Cu:Co atomic ratio was found to be lower, probably due to a partial dissolution of the surface copper species during the strong anodic treatment, particularly for the oxides containing 30 and 40% Li, richer in copper.

XPS analysis revealed that  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Cu}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  are present at the surface of as-prepared and polarized electrodes. Concentration of  $\text{Cu}^{3+}$  species, or probably holes in the  $\text{Cu}^{2+}-\text{O}$  bond, shows a maximum for the 10 and 20% Li compositions to the detriment of  $\text{Cu}^{2+}$  species in the case of fresh electrodes. On the other hand, an increase of the  $\text{Co}^{3+}$  surface concentration is observed for the oxides with higher Li content. We may therefore propose that the introduction of  $\text{Li}^+$  in  $\text{CuCo}_2\text{O}_4$  is predominantly compensated for  $\text{Cu}^{3+}$  ions in the oxides containing up to 20% Li, and for  $\text{Co}^{3+}$  ions in those richer in lithium.

### REFERENCES

1. N. Fradette and B. Marsan, *J. Electrochem. Soc.*, **145**, 2320 (1998).
2. K. Fatih, M. Preda, C. Secours and B. Marsan, submitted to *J. Solid State Chem.*, Dec. 2001.