



Electrocatalytic oxidation of cyanide on copper-doped cobalt oxide electrodes



R. Berenguer^a, A. La Rosa-Toro^b, C. Quijada^c, E. Morallón^{a,*}

^a Instituto Universitario de Materiales, Departamento de Química Física, Universidad de Alicante, Apartado 99, 03080 Alicante, Spain

^b Facultad de Ciencias, Universidad Nacional de Ingeniería, Av. Tupac Amaru, 210 Lima, Peru

^c Departamento de Ingeniería Textil y Papelera, Universitat Politècnica de València, Pza. Ferrándiz y Carbonell, 03801 Alcoy (Alicante), Spain

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ABSTRACT

Copper and copper oxides are well-known excellent catalysts in several chemical processes, but their low mechanical and electrochemical stability restrict their direct utilization as electrodes in electrolytic processes. In this work, the incorporation of copper into cobalt oxide ($\text{Cu}_x\text{Co}_{3-x}\text{O}_4$) is presented as an excellent approach to obtain highly active and robust copper-based electrocatalysts. Particularly, the electrocatalytic performance of Ti-supported $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ electrodes (with $0 \leq x \leq 1.5$) has been studied for the oxidation of cyanide in alkaline media. Cyclic voltammetry and electrolysis runs show an outstanding effect of Cu on the activity, efficiency and kinetics of spinel $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ electrodes for CN^- electro-oxidation. Despite being active oxides with high activity towards water oxidation, copper saturated ($x = 1.0$) and oversaturated ($x = 1.5$) spinels exhibit unprecedented 100% current efficiencies for the electro-oxidation of CN^- in aqueous electrolyte. In situ surface enhanced Raman spectroscopy (SERS) reveals the specific adsorption of CN^- ions on surface Cu species to be involved in the electrocatalytic oxidation mechanism. This electrocatalytic activity has been attributed to surface Cu(II) in the spinel lattice. Furthermore, the $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ electrodes also display high electrochemical stability. Therefore, they are considered excellent candidates for the sustainable electrochemical elimination of highly toxic cyanides.

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1. Introduction

Copper and copper oxides have unique catalytic performance for several chemical processes of major industrial interest [1–5]. In addition, they are very attractive for multiple electrochemical processes and devices [6–11]. Despite such relevance, however, their utilization as electrodes and/or electrocatalysts in electrolytic treatments is greatly restricted by their low mechanical and electrochemical stability [6,11–13]. Hence, the design and development of robust and stable Cu-based electrocatalysts may bring a new generation of active components for multiple electrochemical devices and applications.

Among electrolytic processes, the anodic oxidation of environmental pollutants is considered a powerful technique in wastewater treatment for the abatement (destruction) of refractory and toxic compounds that cannot be removed by conventional biological treatments [14]. A good example of this kind of pollutants is cyanide, which provokes environmental and biological

contamination in surface and ground water [15–17]. Cyanides are widely utilized in large scale industrial processes [16,17] and commonly found in effluents from oil refineries and thermoelectric power stations [16,18], thereby being inevitably released into the environment. As a result, cyanide has been designated as an Environmental Protection Agency (EPA) priority pollutant [19] and proposed to be included in the list of priority substances of the European Union [20], with regulatory agencies imposing discharge limits in the order of <1 ppm [16,21].

Although several physical and chemical methods for cyanide remediation have been reported in the literature [16,21], the electro-oxidation technology gathers several benefits [14]. Basically, it can be conveniently operated in situ, at ambient temperature and pressure, with low energy consumption and short time requirements, just by using electrons as the only reagent. Furthermore, it simultaneously allows the recovery of precious metals on the cathode [14,16]. Nevertheless, the efficiency and cost of the electro-oxidation treatments greatly relies on the choice of a suitable electrocatalyst (anode) [14,22].

Several electrodes including carbon materials [23–26], stainless steel [27], bare Pt and Ni [28,29], boron-doped diamond (BDD) [30], CuO [11], and Ti-supported metal and metal oxide systems (the

* Corresponding author.

E-mail address: morallon@ua.es (E. Morallón).

so-called dimensionally stable anodes, DSA) like PbO_2 [30,31], Pt [28,32], $\text{RuO}_2\text{-TiO}_2$ and $\text{TaO}_2\text{-IrO}_2$ [33], $\text{SnO}_2\text{-SbO}_x$ [34,35], Co_3O_4 [36,37], etc., were previously studied for the direct and indirect electrochemical oxidation of cyanide. However, the reported electrolytic processes by using these anodes showed slow oxidation rates and poor current efficiencies.

Various studies revealed an enhanced cyanide electro-oxidation in the presence of copper. This enhancement was assigned to an electrocatalytic effect caused by copper oxide films in situ deposited on the anode [23–28,31,32]. This catalytic activity is in agreement with the reported promotion of cyanide decomposition by copper species when using other elimination methods [38,39]. Nevertheless, the electrodeposited copper oxide films showed variable low stability and adherence [11,24,31,32], hindering their practical application for electrochemical cyanide destruction.

The design of novel Cu-based electrocatalysts is then receiving increasing attention. Both the catalytic and stability properties of the active copper phase can be greatly influenced by their chemical environment and/or the nature of the support [1–5]. We previously reported the preparation and properties of Ti-supported copper-doped cobalt oxide ($\text{Cu}_x\text{Co}_{3-x}\text{O}_4$) electrodes [40,41]. It was found that Cu(II) is effectively incorporated into the spinel lattice to form a solid solution (monophasic Cu–Co spinel oxide) when the copper content does not exceed that for the stoichiometric CuCo_2O_4 spinel ($x=1.0$). Nevertheless, a new CuO phase segregates on the surface of oversaturated spinels ($x=1.5$). On the other hand, the Cu-doping produces a catalytic effect for the oxygen evolution reaction (OER) in alkaline aqueous electrolyte. This good activity for the OER is expected to be detrimental for the efficiency of the anodic treatment of pollutants [14].

In this work, the electrocatalytic performance of $\text{Ti/Cu}_x\text{Co}_{3-x}\text{O}_4$ electrodes (with $0 \leq x \leq 1.5$) for the oxidation of CN^- is studied in an alkaline medium. This is the medium of choice because of the strongly basic character of cyanide-containing effluent streams from important industrial processes like silver and gold ore extraction, metallurgical processes or electroplating. In addition, a high alkalinity has been proven to obtain better oxidation efficiency [35] and favour the oxidation pathway towards cyanate and subsequent complete mineralization to N_2 and CO_2 [27,35]. The electrochemical behavior of CN^- onto these electrodes is followed by cyclic voltammetry and in situ Raman spectroscopy, whereas its abatement is studied by galvanostatic electrolysis. The electroactivity of the electrodes is then analyzed in terms of current efficiency and kinetics for CN^- electro-oxidation. Results reveal that the introduction of Cu in the cobalt spinel remarkably increases the efficiency and kinetics for CN^- electro-oxidation. Moreover, they suggest that this electrocatalytic effect is related to the specific adsorption and oxidation of CN^- ions on surface Cu(II) placed in the spinel crystalline structure.

2. Experimental

2.1. Preparation and physico-chemical characterization of $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ electrodes

Copper–cobalt spinel oxide electrodes of nominal composition $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ (with $0.0 < x \leq 1.5$) were prepared by thermal decomposition of proper salt precursors onto a Ti support [40]. The salt precursors were made up of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (A.C.S. Aldrich) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (MERCK p.a.) dissolved in absolute ethanol (J.T. Baker). The nitrate salts were mixed in stoichiometric amounts according to the desired nominal composition. The total metallic cation concentration was kept constant at 0.5 M. Prior to the decomposition process, Ti plates ($1 \times 1 \times 0.05$ cm, Goodfellow 99.6%) were degreased in acetone, etched in a boiling 10% oxalic

acid solution for 1 h and finally rinsed with distilled water. The precursor solution was spread over the Ti surface with the aid of a brush. The solvent was dried at 70°C and the electrode was subsequently calcined at 350°C for 10 min, for the thermal decomposition of the salt and metal oxide formation to be accomplished. The Ti sheets were coated with successive layers of the oxides by repeating this procedure. A final annealing step was carried out for 1 h at the same temperature. The most suitable number of deposition steps (about 23) was found to correspond to an oxide loading ranging between 3.00 and 3.50 mg cm^{-2} , as determined by weight difference. For comparison purposes, Ti-supported Co_3O_4 and CuO electrodes were also prepared by the same method. The physico-chemical properties of the electrodes were analyzed in detail in a previous paper [40]. In particular, it should be emphasized that the actual metal cation composition is rather close to the nominal one used in this work to refer to the subscript x (see the [supporting information \(Supp. Info.\)](#)).

2.2. Electrochemical behavior towards CN^- oxidation

2.2.1. Cyclic voltammetry

Electrochemical measurements were carried out at room temperature in a conventional three-electrode cell. The counter electrode was a platinum electrode and the potentials are referred to a reversible hydrogen electrode (RHE) immersed in the same electrolyte. The aqueous 0.1 M NaOH solutions were prepared from Merck p.a. and ultrapure water (Purelab Ultra from Elga-Vivendi, $18.2 \text{ M}\Omega \text{ cm}$), whereas sodium cyanide (Merck p.a.) was used to simulate the CN^- -containing waters of different concentrations. The alkalinity of the electrolyte solution ($\text{pH} = 13$) was high enough to avoid the formation and volatilization of HCN ($\text{pK}_a = 9.21$).

The cyclic voltammograms were obtained at a constant sweep rate of 20 mV s^{-1} . The current densities were calculated using the geometric area of the electrodes (2 cm^2).

2.2.2. Electrolysis runs

Cyanide electro-oxidation experiments were performed galvanostatically in a filter-press cell. Copper-doped cobalt oxides, deposited on titanium expanded meshes (electrode area 20 cm^2), were used as anodes, whereas a stainless steel plate (AISI 310L) electrode of 20 cm^2 was used as the cathode. The starting concentration of cyanide was 500 ppm and an aqueous 0.1 M NaOH solution was employed as the supporting electrolyte. The electrolyte was introduced in a jacketed reservoir and was forced to pass through the undivided cell by means of a centrifugal pump (flow rate = 40.6 mL s^{-1}). Details on the experimental determination of the mass transfer coefficient (k_m) are provided in the [supporting information \(Supp. Info.\)](#). The electrolyte volume was 500 cm^3 and the temperature was controlled at 25°C during the experiment. The applied constant current density was 5 mA cm^{-2} in all experiments. During the constant-current electrolyses, the cyanide concentration was measured by titration with a AgNO_3 standard solution (0.1875 mM) using 5-(4-dimethylaminobenzylidene)-rhodanine as indicator (EPA, 4500-CN-D) [42] and an Ag/AgCl/Cl^- (3M) electrode was used as a reference electrode to monitor the anode potential. The reported cyanide concentration data represent the arithmetic average from three measurements and the current efficiency for the cyanide oxidation was calculated from the decrement of the cyanide concentration in the test solution.

2.2.3. In situ Raman spectroscopy characterization

The electrooxidation of CN^- on $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ electrodes was monitored by in situ Raman spectroscopy. The experiments were performed in a three-electrode spectro-electrochemical cell made of polytetrafluoroethylene (PTFE). More details on this cell can

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