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# Nickel-cobalt-oxide cathodes for hydrogen production by water electrolysis in acidic and alkaline media

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## ABSTRACT

Mixed Ni–Co-oxide cathodes of various compositions were fabricated by a thermal-decomposition method and used as electrocatalysts for hydrogen production by water electrolysis in acidic and alkaline media. The oxide electrodes were found to be of a semi-crystalline structure, yielding the surface morphology characterized by a surface roughness factor going up to 25. Linear potentiodynamic and potentiostatic electrochemical measurements revealed that the Volmer reaction step controlled the kinetics of the hydrogen evolution on all the Ni–Co-oxide cathodes, and also on the pure metal Ni electrode (control). The Ni<sub>0.2</sub>Co<sub>0.8</sub>-oxide was identified as the best electrode material candidate among the investigated metal oxides, which was linked to the surface-area effect. However, its intrinsic activity was found to be lower than that of pure metallic Ni. Nevertheless, the Ni<sub>0.2</sub>Co<sub>0.8</sub>-oxide electrode showed a significantly higher electrocatalytic stability (fouling/deactivation tolerance) in comparison to metallic Ni.

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## Introduction

The demand for novel renewable energy has been increasing over the past few years due to the rapid depletion of the traditional energy sources, such as fossil fuels [1]. Many research efforts have sought ways to reduce the dependency on fossil fuels by trying to find an alternative power source. Hydrogen, the most abundant element in the universe, is considered to be an excellent green energy source due to its minimal impact on the environment [2]. Despite its abundance, hydrogen is hardly found as a separate element. Instead, it is primarily found in combination with carbon in hydrocarbon compounds, and with oxygen in water [3].

Hydrogen (H<sub>2</sub>) can be obtained by water electrolysis, where electrical current is applied to split water into its components (oxygen and hydrogen). Hydrogen obtained by water electrolysis is a clean energy carrier since it can produce energy in fuel cells (or by burning) without emitting carbon dioxide [4]. Unfortunately, water electrolysis is not yet cost-competitive to hydrocarbon reforming due to its high operational costs (electricity cost, electrode degradation). In the case of production of hydrogen by polymer-electrolyte-membrane (PEM) electrolyzers, the operational costs per amount of produced hydrogen are lower in terms of the electricity used, but the cost of the PEM technology is higher in comparison to the conventional alkaline electrolyzers. This is mainly a consequence of the use of expensive noble metals (platinum,

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ruthenium, and iridium) as electrocatalyst (electrode) materials, which are required due to the high acidity of the electrolyte environment [5]. In addition, despite the use of noble metals, the long-term stability and activity of electrodes are still not satisfactory. On the other hand, in alkaline electrolyzers, nickel electrodes could be used because of a much milder electrolyte environment (high pH). However, neither currently-used nickel electrodes offer satisfactory performance, especially regarding the fouling susceptibility (deactivation of Ni cathodes by electrochemically deposited trace metals) and mechanical stability. Also, further decrease in the hydrogen evolution reaction (HER) overpotential is required to make this process feasible.

An ideal electrode for the HER should have characteristics such as low overpotential, large active surface area, physical and electrochemical stability, high fouling resistance, low-cost, ease of use, and excellent electrical conductivity [6]. In this context, extensive research has been performed on the development of new electrode materials for hydrogen production [5–17]. Ni-based alloys have been identified as suitable candidates for electrodes in the alkaline water electrolysis, and in particular, Ni–Co has been found to offer electrocatalytic activity comparable to that of noble metals [16,18–22].

Unfortunately, pure metallic Ni-based alloys suffer two significant drawbacks. First, they cannot operate in PEM water electrolyzers due to their poor corrosion stability in the acidic medium. Second, they are susceptible to deactivation by electrodeposition of metallic impurities presented in the electrolyte, and thus their long-term stability and activity are not satisfactory even in alkaline water electrolyzers [23]. In the search for new materials, certain metal oxide electrodes have demonstrated excellent performance in the hydrogen evolution reaction, but they have not been widely studied [6,23,24]. The most intriguing aspect of metal oxides is that they have the ability to remain active for HER even in the presence of metallic impurities [23]. Furthermore, oxide electrodes have been claimed to be stable in both acidic and alkaline environments [25]. Due to the unique features of the metal oxides, they have been recognized as promising cathode materials for the electrocatalysis of HER [26].

The purpose of this research was to develop and study mixed Ni–Co-oxide cathodes for hydrogen production by water electrolysis in both the acidic and alkaline media. The rationale for choosing Ni–Co-oxides was due to their availability, low-cost, and promising results obtained in previous research studies as pure (non-oxide) alloy cathodes for hydrogen evolution [5,23]. The objective of this study is to report the effects of electrode composition and electrolyte temperature on the electrocatalytic performance for the HER.

## Experimental procedure

### Electrode preparation

Ni<sub>x</sub>Co<sub>(1-x)</sub>-oxide coatings (x = 0, 0.2, 0.4, 0.6, 0.8, 1; where x is the molar fraction and refers to the content of Ni and Co in the precursor solution) were formed on a flat titanium substrate by

employing a thermal-decomposition method. A titanium button-shaped plate of 1.27 cm in diameter (purity 99.2%, Alfa Aesar, USA), with a thickness of 0.2 cm was used as the substrate. A first step of the electrode preparation process was to wet-polish the titanium substrate using 600-grit SiC sandpaper. Next, the polished plate was rinsed thoroughly and sonicated for 30 min in deionized water (resistivity 18.2 MΩ cm) to remove polishing residues. Then, the plate was etched in a boiling solution of hydrochloric acid (37 wt%, Fisher Scientific, Canada) and deionized water (1:1 by volume) for 30 min. After etching, the plate was again thoroughly rinsed with deionized water, and dried in argon gas (MEGS Specialty Gases Inc., 99.998 wt% pure, Canada).

To coat the titanium plate, a 0.2 M precursor solution was prepared by dissolving the metal precursor salts in an equi-volume mixture of 37 wt% hydrochloric acid and deionized water. NiCl<sub>2</sub> × 6H<sub>2</sub>O (purity 99.9%, Sigma-Aldrich, Canada), and Co(NO<sub>3</sub>)<sub>2</sub> × 6H<sub>2</sub>O (purity 99.7%, Acros Organics, Canada) were used as a source of nickel and cobalt, respectively. The coating solution was applied uniformly to the titanium substrate with a paintbrush (only one side of the titanium plate was coated with the precursor solution). After applying the first layer, the sample was placed in an oven at 383 K for five minutes to vaporize the solvent, followed by annealing the sample at 773 K in an air-natural-convection furnace for fifteen minutes. Next, the sample was removed from the furnace and allowed to cool for ten minutes, before another coating was applied. This same procedure was repeated six times to form a six-layered coating on the titanium substrate. Lastly, the sample was annealed in the furnace at 773 K for one hour to complete the oxidation of the coating to produce the Ni<sub>x</sub>Co<sub>(1-x)</sub>-oxides.

### Electrochemical and surface/chemical composition characterization

The electrochemical characterization of electrodes towards hydrogen evolution reaction was investigated using a three-electrode cell, at 293 ± 2 K and atmospheric pressure. The working electrode (WE) was at the bottom of the cell, fitted between a steel plate (to provide electrical contact) and the Teflon base of the cell containing an opening to the electrolyte. The geometrical area of the electrode exposed to the electrolyte solution was 0.68 cm<sup>2</sup>. The counter electrode (CE), a graphite rod, was placed inside a glass tube plugged with a glass frit (Ace Glass Inc., USA) which prevented O<sub>2</sub> gas produced at the CE (anode) to migrate towards the WE and get reduced, thus interfering with the HER. A saturated calomel electrode (SCE) (Accumet electrode, Fisher Scientific, USA) was used as the reference electrode (RE). To maintain an oxygen-free electrolyte solution, the solution was purged by argon gas for 30 min before electrochemical measurements and continued to be purged during the measurements. In order to characterize the electrochemical behavior of the coatings, linear Tafel polarization (LTP), chronoamperometry (CA), chronopotentiometry (CP) measurements were performed using an Autolab PGSTAT30 potentiostat/galvanostat with NOVA software (v. 2.1; Metrohm, the Netherlands). Electrochemical measurements were done using two different electrolytes: 0.5 M H<sub>2</sub>SO<sub>4</sub> (pH = 0.25) for the acidic

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