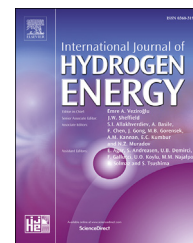


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Oxygen evolution catalysis in alkaline conditions over hard templated nickel-cobalt based spinel oxides

Paweł Stelmachowski ^{a,b,**}, Alessandro H.A. Monteverde Videla ^{a,*},
Klaudia Ciura ^b, Stefania Specchia ^a

^a Politecnico di Torino, Dept. of Applied Science and Technology, Corso Duca Degli Abruzzi 24, 10129, Torino, Italy

^b Jagiellonian University in Kraków, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland

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ABSTRACT

In this work, two series of cobalt-based spinel catalysts, Co_3O_4 and NiCo_2O_4 , were synthesised by a hard template method with SBA-15 and were investigated as non-noble catalysts for the oxygen evolution reaction (OER) under basic conditions. The effect of synthesis conditions, i.e., heating rate and calcination temperature, and the addition of minor amounts of iron were evaluated with respect to the OER activity. Moreover, the influence of the alkali cation type in the electrolyte (Li, Na, K) was also evaluated. The highest activity was found for the NiCo_2O_4 obtained with the lowest heating rate. The increase in the heating rate and calcination temperature results in the decrease of the available surface area for the reaction, leading to the deterioration of the activity. The incorporation of 3 wt% of iron in the lattice of NiCo_2O_4 and Co_3O_4 resulted in a decrease of the OER activity, however, the deactivation was much less severe in the case of NiCo_2O_4 than for Co_3O_4 . Among the alkaline electrolytes used, KOH resulted in the highest catalytic activity both for NiCo_2O_4 and Co_3O_4 .

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Introduction

Hydrogen is an energy vector that can be used either to produce power by a suitable electrochemical conversion (fuel cells technology) or as a reagent for other chemicals. The electrolysis of water is a clean way to produce hydrogen and oxygen, without production of contaminant gases, avoiding further separation systems. This reaction is not

spontaneous, and thus requires the use of catalyst and energy input. The development of cheap catalysts, based on abundant raw materials, capable of competing with active but expensive noble metal-based catalysts, has been in the focus of the water electrolysis research during the last years [1]. From a sustainability point of view, electro-splitting of water is only a feasible option when electricity is coming from non-convictional sources, avoiding methane reforming

* Corresponding author.

** Corresponding author. Politecnico di Torino, Dept. of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129, Torino, Italy.

E-mail addresses: pawel.stelmachowski@uj.edu.pl (P. Stelmachowski), alessandro.monteverdevidela@polito.it (A.H.A. Monteverde Videla).

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or coal gasification [2]. Electrochemical water splitting is associated with a substantial energy loss, mainly due to the stability of water and high over-potentials at the oxygen-evolving anode.

Currently, the best performing electrocatalysts are the Ru-oxides and Ir-oxides in acidic electrolyte, but the cost and scarcity of these materials renders them impractical for large-scale water electrolysis systems [3–6]. Fortunately, earth-abundant and inexpensive Ni and Co electrocatalysts in alkaline electrolyte have been shown to exhibit comparable performance to Ru-oxide and Ir-oxide electrocatalysts in an acidic electrolyte. The incorporation of mobile Fe species would lead to an increase of electrochemical activity by modifying the strength of O–Ni–O bonds [7].

First-row transition metals, specifically spinel and perovskite oxide materials exhibit encouraging activities in basic conditions, especially those based on cobalt and nickel with the addition of iron [8]. These metals fulfil the requirement of a low-price, readily available source for the large-scale use. Their beneficial characteristics include rich surface chemistry, related to the availability of different oxidation states and hydroxylation degree, stability in alkaline conditions and appreciable electrical conductivity. The spinel and perovskite structures allow for fine tuning of the chemical composition and resulting electronic properties, which is the basis for their catalytic activity. Recent research underlines the effect of intentional (doping) or unintentional (incidental) incorporation of iron into the nickel based catalysts [8–12]. The observed dramatic increase of reactivity was ascribed to a Fe-induced partial-charge-transfer mechanism, which would activate the nickel centres throughout the catalyst film [10]. Despite its beneficial promoting effect, iron-based materials exhibit relatively low electrocatalytic activity due to their negligible effective electrical conductivity, especially at low overpotentials [9].

Current efforts on the catalysts development for OER are focused on oxide and hydroxo-oxide materials [9], in particular, on those containing nickel, in order to boost activity and further improve stability. Table 1 shows an overview of the most recent reports on NiCo_2O_4 based OER electrocatalysts. As evidenced by the data collected in Table 1 and our previous report, regarding Co_3O_4 obtained with different synthesis methods [13], not only chemical composition and structure determine the catalytic activity, but also the morphology of the catalyst is an important factor [14]. The porous structures can be obtained using, e.g., the hard template method, but the final properties depend not only on the template but also on the conditions applied. In addition, the presence of Fe impurities, usually present in neutral to alkaline electrolytes, may substantially enhance the activities of Ni and Co-based OER catalysts [8,9,15]. However, the level of doping plays a key role, since FeO_xH_y materials are typically not considered to be good OER catalysts [9].

The heating rate, maximum temperature attained during the calcination, cooling rate, and atmosphere during the synthesis determine the final morphology of the produced catalyst and thus influence its catalytic activity. The aim of the study was to evaluate the effect of hard template synthesis conditions with SBA-15 (Santa Barbara Amorphous 15, a silica with pore size of 4.6–30 nm) and iron addition on the catalytic

oxygen evolution activity of a series of cobalt and nickel-cobalt spinel based oxides.

Experimental

Chemicals

Cobalt(II) nitrate hexahydrate ($\geq 98\%$ purity), nickel(II) nitrate hexahydrate ($\geq 99\%$ purity), iron(III) nitrate nonahydrate ($\geq 99.95\%$), isopropanol 99.8 wt%, Nafion[®] solution containing 5 wt%, tetraethyl orthosilicate 98%, Pluronic[®] P-123, potassium hydroxide 85 wt%, lithium hydroxide monohydrate (99.95%), sodium hydroxide ($\geq 98\%$), hydrofluoric acid 48 wt%, were purchased from Sigma–Aldrich. Aqueous solutions were prepared using ultrapure water obtained from a Millipore Milli-Q system with a resistivity $\sim 18 \text{ m}\Omega \text{ cm}$. Pure air and nitrogen gases (purity 99.999%) were supplied in compressed cylinders provided by SIAD company and used as received.

Catalysts preparation

NiCo_2O_4 by SBA-15 hard template method was synthesised as described by Zheng et al. [16]. Cobalt and nickel nitrates were dissolved in acetone and impregnated over in-house prepared SBA-15 mesoporous silica powder leaving it to dry at 70°C , in an ultrasonic bath. Then, the dried powder was ground using a mortar and calcined at 380°C for 4 h in static air. Two different furnace heating rates (β) were used for Ni–Co materials: 1°C min^{-1} and 4°C min^{-1} . Additionally, in order to induce NiO segregation, one sample was heated at 4°C min^{-1} up to 550°C and annealed for 4 h in static air. Finally, the obtained powders were dispersed in a 5 wt% hydrofluoric acid and stirred for 24 h, to remove the SiO_2 template. The obtained material was thoroughly rinsed on a Buchner funnel with deionised water, in order to remove any trace of F^- . Moreover, two samples with addition of 3 wt% of iron were prepared in the same way, with calcination at 380°C and heating rate of 1°C min^{-1} .

Physicochemical characterization

Specific surface areas (SSA) were obtained by N_2 adsorption-desorption using the Brunauer–Emmet–Teller (BET) method within the relative pressure range of 0.1–0.3 on an ASAP 2020 C Micromeritics Instrument. Prior the adsorption, samples were evacuated at 150°C for 3 h under low vacuum. The desorption cumulative volume of pores was obtained with the Barrett–Joyner–Halenda (BJH) method.

XRD patterns were obtained with the use of a Rigaku MiniFlex powder diffractometer with $\text{Cu K}\alpha$ radiation at 10 mA and 10 kV, 2 θ step scans of 0.02° , and a counting time of 1 s per step. The X-ray diffraction lines characteristic of the spinel structure were indexed with the Fd3m space group (24210-ICSD). Micro-Raman spectra were recorded using a Renishaw InVia spectrometer, with a Leica DMLM confocal microscope, a CCD detector, and using 514 nm excitation wavelength. The Raman scattered light was collected in the spectral range $100\text{--}900 \text{ cm}^{-1}$, with a $50\times$ magnification lens. At least nine

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