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Ni-Fe-Cr-Oxides: An Efficient Catalyst Activated by Visible Light for the Oxygen Evolution Reaction

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Abstract: The oxygen evolution reaction (OER) is a thermodynamically and kinetically demanding process, therefore it requires the use of catalysts enabling to meet technologically relevant conditions. Here, we realized efficient OER catalysts fabricated using relatively cheap precursors consisting of earth-abundant metal oxides, i.e. nickel, iron, and chromium, and a simple one-step preparation method. It is shown that the catalyst is activated by anodic polarization under irradiation with visible light, which allows decreasing the overpotential necessary for the OER.

Keywords: metal oxide, oxygen evolution reaction, photoelectrocatalysis, rutile.

1 Introduction

One of the important goals of continuing research efforts for the replacement of fossil fuels with renewable energy sources is finding efficient materials to allow sustainable and carbon-neutral storage of solar energy [1]. For this purpose, the

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efficient electrochemical, photocatalytic or photoelectrochemical water splitting into hydrogen and oxygen is required [2–5]. However, from the perspective of a large-scale hydrogen production, while the hydrogen evolution reaction is a relatively easily catalysed process, the main issue is the sluggish kinetics of the 4-electron oxygen evolution reaction (OER) [6–8]. Therefore, catalytic materials are needed to minimize the energetic losses, i.e. the overpotential required for the OER. In addition, the catalysts should consist of highly available elements and, subsequently in the form of electrodes, remain stable under operation at strongly oxidizing conditions [9–11].

In this context, transition metal oxides have emerged as a promising class of materials, mostly due to low cost, abundance, and particular redox properties, promoting their successful use in commercial electrolyzers [12–14]. In comparison with single-metal oxides, mixed metal oxides have shown an enhanced catalytic activity. In particular, oxides/hydroxides containing both Fe and Ni exhibit a significantly higher activity than other single-metal compounds [3, 15–17]. Although the true reason of this synergy is not yet fully understood, Chen et al. [18] reported recently direct evidence from Mössbauer spectroscopy about the formation of Fe^{4+} species in this type of catalysts, while the Fe^{4+} ions were absent in a catalyst consisting only of iron compounds. The authors suggested that the OER involves active sites generated at defect sites, including edges and corners within the NiOOH lattice doped with Fe.

Addition of a third metal along with nickel and iron can also lead to an improved activity towards the electro-oxidation of water in alkaline solutions [9, 19]. The increase in electrocatalytic activity of the catalyst may be associated with a modification of the electronic properties of the material in favour of the O_2 evolution and can be also ascribed to an increase in the specific surface area/roughness factor of the prepared oxides.

Herein, we present the preparation and characterization of an OER catalyst composed of nickel, iron, and chromium oxides deposited onto a transparent conductive oxide, F-doped SnO_2 (FTO) used as a substrate. In particular, we show for the first time that the synthesized catalyst undergoes activation under preliminary polarization performed under visible light illumination. Moreover, we also report that such Ni-Fe-Cr electrocatalysts exhibit a favourable effect on the visible-light driven oxidation of water on a TiO_2 photoanode.

2 Results

Electrochemical evaluation of the fabricated Ni-Fe-Cr electrocatalyst composed of three different oxides (NiO , $\gamma\text{-Fe}_2\text{O}_3$, and Cr_2O_3 , in a 1:2:1 volume ratio) deposited

onto an FTO substrate provided, as expected, a large increase in the measured current for O_2 evolution in comparison with the bare substrate. Figure 1 summarizes the current-voltage plots recorded in a 0.1 M NaOH solution. As it can be observed (Figure 1, red trace), the OER current reaches 1.5 mA cm^{-2} at a potential of 1.8 V vs. RHE and the reaction shows a detectable current increase at a potential of ca. 1.55 V vs. RHE. The observation of increased currents and photocurrents was confirmed to be direct consequence of O_2 production from water splitting by means of scanning photoelectrochemical microscopy (Figure 1b). A Pt microelectrode was used for the collection of locally generated O_2 at the catalyst-coated sample. After polarization of the sample to a highly anodic bias, a significant increase of the measured cathodic tip current was observed, verifying the presence of O_2 evolution.

The obtained results are consistent with the corresponding Tafel plots (see Figure 2). Rather unexpectedly, the as-prepared Ni-Fe-Cr-oxide modified FTO-electrodes did not only work as electrocatalyst but also initially exhibited significant photocurrents under simulated solar irradiation (Figure 1, blue trace).

Further experiments indicated the possibility of improving the activity of the prepared electrodes by an initial polarization at anodic potentials with simultaneous exposure to simulated solar radiation leading to an increased sample activity for the OER both in the dark and under continuous illumination. Applying this pre-treatment (imposing both an anodic potential and illumination), provided a notable increase in OER photocurrent to up to 2.75 mA cm^{-2} at a potential of 1.8 V

Fig. 1: (a) Current density-potential (j - E) plots for a bare FTO electrode (black) and a catalyst-coated FTO recorded in the dark (red) and under irradiation during measurement with simulated AM 1.5 light (blue). Dashed lines represent plots recorded after applying a potential of 1.7 V vs. RHE for 60 min to the electrode. (b) Current obtained at a Pt microelectrode tip utilized for O_2 detection above the surface of a catalyst-coated FTO. Pt microelectrode (25 μm diameter). Tip-to-sample distance: 13 μm . Local irradiation of the sample at an incident power of 100 mW cm^{-2} . Measurements were conducted in 0.1 M NaOH.

Fig. 2: (a) Comparison of Tafel plots obtained for a bare FTO electrode (black) and catalyst-coated FTO electrodes (red and blue) recorded in the dark. The blue curve was recorded after applying to the electrode a potential of 1.7 V vs. RHE for 60 min. Measurements were conducted in 0.1 M NaOH. (b) Tafel parameters for bare FTO and catalyst-modified electrodes extracted from the results showed in part (a) of the figure.

vs. RHE and made possible to lower the overpotential needed for the reaction by *ca.* 0.110 V (see Figure 1).

Sample characterization by means of SEM revealed that the catalyst formed small crystallites of around few nm in size on the surface of larger FTO crystals (Figure 3b). The elemental mapping analysis carried out by energy dispersive X-ray spectroscopy (EDX, see Figure 4) suggests that the individual metals are evenly distributed at the sample surface.

Furthermore, in order to gain information about the structure and chemical composition of the prepared catalysts we conducted powder X-ray diffraction analysis (PXRD). Despite the X-ray fluorescence of iron atoms (Cu $K\alpha$ incident radiation exceeds the energy of the K absorption edge of Fe), the PXRD pattern of a mixture of Fe, Ni, and Cr oxides was collected. Figure 3a shows the correlation between experimental data and theoretical PXRD patterns for structures of NiO (*Fm-3m* space group) [20], $\gamma\text{-Fe}_2\text{O}_3$ (*Fd-3m* space group) [21], and Cr_2O_3 (*R-3c* space group) [22]. The sharp reflections belong to the Cr_2O_3 phase and their full width at half maximum (FWHM) indicates the presence of crystallites with a well-defined diameter. Other peaks can be recognized as $\gamma\text{-Fe}_2\text{O}_3$ and NiO phases with high FWHM values. The sizes of the crystallites for the latter two phases are relatively smaller in comparison with that for the Cr_2O_3 phase (see below). Formation of crystallites was observed during the heat treatment of the sample. Moreover, growth was observed after activation by anodic potential in the presence and absence of light but not under light only.

Fig. 3: (a) Powder XRD diffraction patterns of the Ni-Fe-Cr catalyst and nickel, iron and chromium oxides. (b) SEM images of an FTO substrate covered with the Ni-Fe-Cr catalyst as-prepared (*top*) and after full activation by applying an anodic potential and illumination (*bottom*).

Fig. 4: EDX images of the catalyst layer deposited on an FTO substrate showing an even distribution of the individual metals on the sample surface.

To monitor the changes in morphology of the catalyst induced by the activation treatment, we performed SEM imaging of the electrode activated by potential and light treatment (Figure 3b, lower panel) and XRD measurements of the

Fig. 5: Powder XRD patterns obtained for an as-prepared Ni-Fe-Cr catalyst and the same catalyst after potential and simultaneous potential and light treatments.

samples after only potential treatment and after simultaneous potential and light treatment (Figure 5). Comparison of the obtained diffraction patterns for the as-prepared and activated catalyst revealed very similar results, indicating no change in phase composition. However, an increased intensity of certain peaks observed in the samples after both pre-treatment conditions, i.e. anodic applied potential and anodic applied potential under irradiation with an AM 1.5 simulated light, suggesting an improvement in crystallinity. This was consistent with the changes observed in the average crystallite diameter (see Table 1), which generally rises after each activation step.

The activating effect of the imposed anodic potential (at 1.7 V vs. RHE) is only observed for electrodes containing Ni, and is likely to be associated with the

Tab. 1: Average crystallite diameter of the particles calculated from the diffractograms presented in Figure 5.

Sample	Average crystallite diameter (nm)		
	$\gamma\text{-Fe}_2\text{O}_3$	Cr_2O_3	NiO
As-prepared	5.2	32.1	7.1
Potential treatment	6.2	39.4	8.4
Potential and light treatment	6.4	42.1	9.8

Fig. 6: (a) Current density-potential (j - E) plots for NiCr catalyst-coated FTO recorded in the dark (black) and under simulated solar radiation, chopped light (light on/off every 5 s) (red) (b) j - E plots for FeCr catalyst-coated FTO recorded in the dark (black) and under simulated solar radiation (light on/off every 5 s) (red). Dashed lines represent plots recorded after applying to the electrode a potential of 1.7 V vs. RHE for 60 min. The insets present an expanded region of the plots for potentials lower than the OER, showing light sensitivity for samples containing iron oxide (panel b). Measurements were conducted in 0.1 M NaOH.

electrochromic behaviour of nickel oxide (Figure 6). It is known that NiO can form coloured NiOOH by oxidation in alkaline electrolyte [23]. Additional measurements recorded under chopped light irradiation showed also, that the presence of Fe in the catalyst determines the presence of exhibited photosensitivity (*cf.* differences in the j - E curves in Figure 6a and b). This observation may be compared with a recent report from Hur et al. [24] showing noticeable water splitting photocurrents for a maghemite/reduced graphene oxide nanocomposite. In fact, the photocurrents observed for the Ni-Fe-Cr catalyst certainly reflect the photoconductivity due to the presence of maghemite [25]. Although after full activation the Ni-Fe-Cr modified electrode no longer exhibits light sensitivity, transformation of $\gamma\text{-Fe}_2\text{O}_3$ into a different iron oxide is not expected but rather the fact that a small photocurrent is hidden below the significantly increased total current dominated by the OER.

In addition, it is well known that under continuous oxidative voltammetric cycling, NiO undergoes morphological changes leading to a more open structure of the oxide [23]. Considering our results, irradiation of the Ni-Fe-Cr oxide layer with visible light during potential application seems to intensify this effect. As can be seen in the SEM image after activation of the catalyst (Figure 3b), activation promotes direct contact between nanoparticles of the different oxides as a result of crystallite growth, that also improves the flow of current within the discontinuous catalyst layer. Most likely, the growth of crystallites leading to a more intimate contact between particles contributes to an increased conductivity of the material.

Interestingly, after deposition of the Ni-Fe-Cr-oxide catalyst as a top layer over the surface of a photoanode made of titanium dioxide (rutile), a large increase in the water splitting photocurrent of ca. 30% is observed, alongside with a slight shift of the open circuit potential measured under simulated solar radiation (Figure 7a). The deposited catalyst provides also an enhancement in the measured incident photon-to-current conversion efficiency (IPCE) in the visible region of the spectrum (Figure 7b).

To conclude, we have realized an efficient OER catalyst containing earth-abundant metal oxides in the form of small crystallites, uniformly distributed at the sample surface. The catalyst is composed of three different oxides (NiO, γ - Fe_2O_3 , and Cr_2O_3), and exhibits enhanced catalytic activity in comparison with single-metal oxides and their binary composition (Figure 8). The activity of the catalyst can be further increased by applying an anodic pre-polarization and irradiation with visible light. This enhanced activity is the result of crystallite growth

Fig. 7: (a) Evolution of the photocurrent density of a TiO_2 photoanode before (black) and after (red) the deposition of a Ni-Fe-Cr-oxide catalyst top layer. (b) Incident photon-to-current conversion efficiency (IPCE) spectra for TiO_2 (black) and Ni-Fe-Cr catalyst-covered TiO_2 (red) in the visible range of light (420–600 nm). The inset shows the full IPCE spectra. Measurements were conducted in 0.1 M NaOH under simulated AM 1.5 illumination (100 mW cm^{-2}).

Fig. 8: (a) Current density-potential (j - E) plots for various compositions of catalyst-coated FTO recorded under simulated solar radiation (without activation process). Measurements were conducted in 0.1 M NaOH.

as confirmed by XRD measurements, which enables direct contact between crystallites leading to the increased conductivity and lower resistivity of the film. Deposition of the catalyst onto a photoanode made of TiO_2 (rutile) results in substantially increased water splitting photocurrents.

3 Experimental section

The method used for preparation of the catalyst was adapted from ref. [11]. First, aqueous precursor solutions (with 9 vol% of glycerol added) were prepared from Ni, Fe, and Cr nitrates (5 mM in metal), mixed in a volume ratio of 2:1:2, respectively, and deposited onto a conductive F-doped SnO_2 (FTO) or TiO_2 substrate by means of the doctor blade technique. Note that this composition was earlier reported to be highly active towards water electro-oxidation in alkaline solutions [9, 26]. Afterwards, the prepared samples were annealed in an electric kiln at 500 °C for 6 h.

Titanium dioxide electrodes were prepared by oxidizing previously etched Ti plates in air at 550 °C [27].

Diffraction patterns were collected using a Bruker D8 Discover diffractometer with Debye-Scherrer geometry. The measurements were performed using Cu

K α radiation ($\lambda = 1.540598 \text{ \AA}$) at a scan rate of $1^\circ/\text{min}$ in 0.012° steps, covering a range of 2θ from 8° to 130° . Samples were measured at room temperature.

Scanning electron microscopy (SEM) imaging of the samples was performed using a Carl Zeiss AURIGA CrossBeam workstation.

(Photo-)electrochemical measurements were performed in a three-electrode configuration using a Teflon cell equipped with a quartz window. All working electrodes had an exposed surface area of 0.28 cm^2 , a Pt wire served as counter electrode and the potentials were controlled against an Ag/AgCl (3 M KCl) reference electrode. The experiments were carried out using a Biologic model P-300 electrochemical analyser. For sample irradiation an Oriel solar simulator featuring a 150 W Xenon lamp and an air mass filter (AM 1.5) was used. The IPCEs of the TiO_2 and NiFeCr/TiO_2 electrodes were determined using light from a 150 W Xenon lamp passed through a monochromator with a bandwidth of 10 nm. The absolute light intensity was measured with an OL 730-5C UV-enhanced silicon detector (Gooch & Housego).

Detection of O_2 formed during the water splitting process was performed by means of scanning photoelectrochemical microscopy [28]. A Pt tip polarized at an adequate potential for O_2 reduction ($-600 \text{ mV vs. Ag/AgCl/3 M KCl}$) was placed in close proximity to the sample surface. During the measurement, the potential applied to the sample was switched between a non-action potential (0.97 V vs. RHE) and a potential for O_2 evolution (1.97 V vs. RHE) according to the obtained LSV results.

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