



Electrocatalytic activity of CoFe_2O_4 thin films prepared by AACVD towards the oxygen evolution reaction in alkaline media

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ABSTRACT

The electrocatalytic behaviour of CoFe_2O_4 thin films, prepared by aerosol-assisted chemical vapour deposition, towards the oxygen evolution reaction in an alkaline medium is reported. X-ray diffraction and SEM data show that the CoFe_2O_4 thin films are phase pure and consist of dendrites 0.5–1 μm in diameter rising from the surface with heights ranging from 1 to 3 μm . The CoFe_2O_4 thin films exhibited an overpotential of 490 mV at a current density of 10 mA cm^{-2} , and a Tafel slope of 54.2 mV dec^{-1} . Taking into account the electrochemically active surface area, the intrinsic activity of CoFe_2O_4 was found to be $1.75 \text{ mA cm}_{\text{real}}^{-2}$ at an overpotential of 490 mV. The CoFe_2O_4 thin films were highly stable and were capable of maintaining catalytic activity for at least 12 h.

1. Introduction

The global increase in the demand of energy, depletion of fossil fuels and increased environmental concerns has sparked research into clean and sustainable alternative energy sources [1]. Hydrogen is considered a fuel for the future as it does not result in the release of carbon emissions to the environment; however, there is still a need for a clean, reliable and sustainable method for its large scale production in order for it to be used as a fuel [2]. Water electrolysis to produce hydrogen offers a simple way to store energy generated from intermittent sources such as wind and solar energy. Commercial electrolyzers are becoming widely available due to rapidly increasing demand for hydrogen and clean water [3,4]. Unfortunately, the major obstacle to achieving efficient water electrolysis is the large overpotential required for the oxygen evolution reaction (OER) [5]. This is therefore the most energy intensive step in water electrolysis. A low-cost and efficient electrocatalyst is thus required to minimize the energy needed in this step [5]. In terms of long-term stability of practical devices, water electrolysis in alkaline media is becoming more attractive [5].

At present, RuO_2 and IrO_2 electrocatalysts exhibit the lowest overpotential for the OER at practical current densities; however, the high cost of these materials and poor long-term chemical stability in alkaline media means their use as anodes in water electrolyzers is not economically viable [6–8]. In recent years, Co has attracted significant attention for its activity towards the OER due its abundance. Various Co containing compounds, such as, oxides [9–11], phosphates [12,13], perovskites [14], and (oxy)hydroxides [15] have shown good OER activity. Fe is another abundant element; whilst iron oxide ($\alpha\text{-Fe}_2\text{O}_3$) has

been extensively studied for photoelectrochemical water oxidation [16], comparatively little work has been carried out on its use as an OER electrocatalyst in an alkaline media [17]. It has been generally established that transition metal oxides often form (oxy)hydroxides at their surfaces in alkaline conditions. A recent report has found that in CoFe oxyhydroxides, Fe is the most active site, whilst the CoOOH provides a conductive support, resulting in a synergistic effect towards catalysing the OER [5].

In this communication, we report the electrocatalytic activity of spinel CoFe_2O_4 prepared by low-cost aerosol-assisted chemical vapour deposition (AACVD) towards the OER in an alkaline medium. The advantage of using AACVD to prepare thin films of electrocatalysts is that it requires no binders, hence undesirable effects such as stability failure or decrease in conductivity can be easily avoided [18]. CoFe_2O_4 displays an overpotential of 490 mV at a current density of 10 mA cm^{-2} in 1 M NaOH, and a Tafel slope of 54.2 mV dec^{-1} . The CoFe_2O_4 thin films were highly stable, only exhibiting an overpotential increase of 0.06 V after a 12 h galvanostatic stability test at 10 mA cm^{-2} .

2. Experimental

2.1. Thin film fabrication

CoFe_2O_4 thin films were prepared by AACVD as reported previously [19]. The AACVD precursor solution was made by dissolving iron (III) acetylacetonate and cobalt (II) acetate in methanol to give concentrations of 0.1 M and 0.05 M, respectively. F:SnO_2 coated glass was used as the conducting substrate (TEC 8 NSG, $8 \Omega/\square$), which was cut in to

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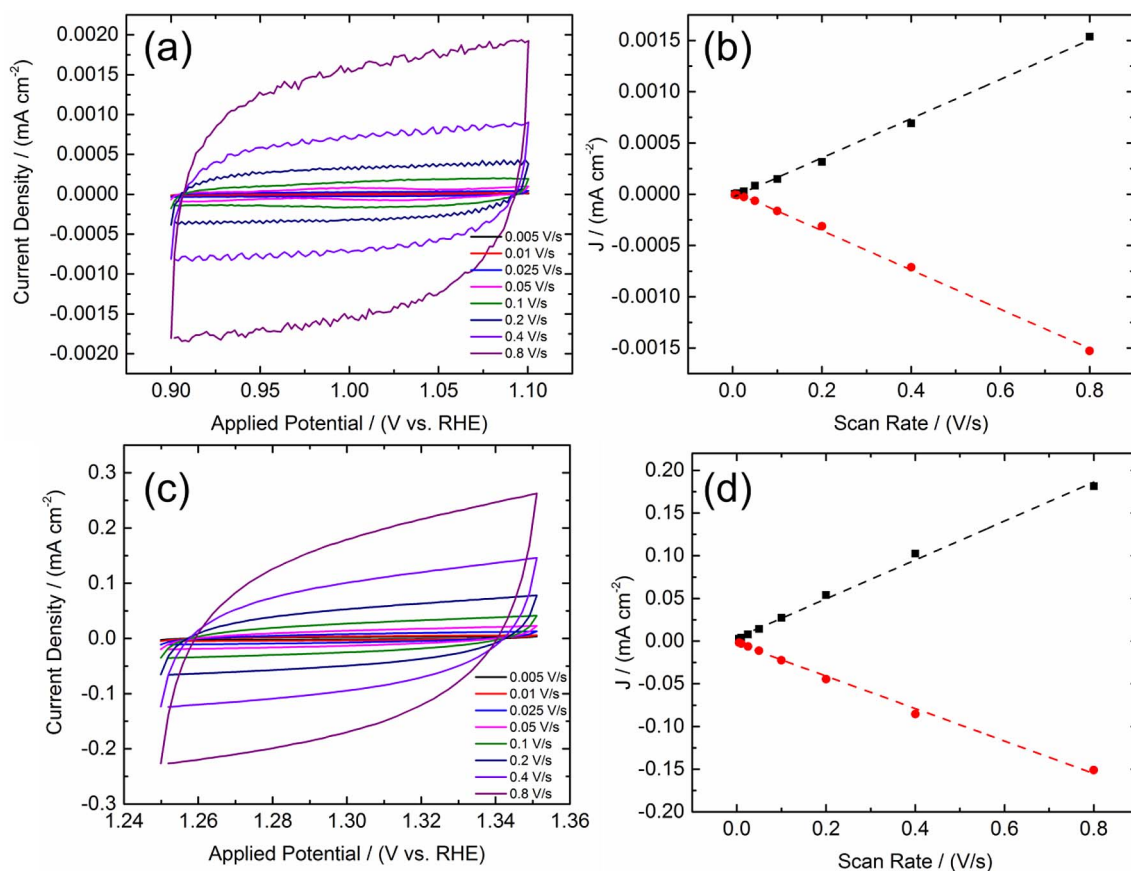


Fig. 1. Determination of differential capacitance of CoFe₂O₄ and the substrate (F:SnO₂) from cyclic voltammetry measurements as a function of scan rate in 1 M NaOH. Cyclic voltammograms of (a) F:SnO₂ and (c) CoFe₂O₄ between scan rates of 5 mV s⁻¹–0.8 V s⁻¹. Anodic and cathodic current density vs. scan rate for (b) F:SnO₂ and (d) CoFe₂O₄ at a potential of 1 V and 1.3 V, respectively.

1 × 2 cm pieces and ultrasonically cleaned in distilled water, acetone, isopropanol and then stored in ethanol. Prior to deposition by AACVD, the glass substrates were placed on a hotplate set to 500 °C for 10 min to allow its temperature to be equilibrated with the surface of the hotplate. The precursor solution was placed in a two-necked round bottomed flask, and an aerosol of the solution was generated using an ultrasonic humidifier. This aerosol was transferred to a second flask using air as a carrier gas at a flow rate of 175 ml min⁻¹. From the second flask, the aerosol stream was directed towards the heated substrate at a flow rate of 2340 ml min⁻¹. The deposition process was carried out at 500 °C for 20 min, after which the coated substrate was removed from the hotplate and allowed to cool to room temperature.

2.2. Material and electrochemical characterisation

All electrochemical measurements were carried out using an Autolab PGSTAT12 potentiostat. Three-electrode measurements were conducted in 1 M NaOH (semiconductor grade, 99.99% trace metals basis, Sigma Alrich) using a Pt gauze counter electrode and Ag|AgCl reference electrode. For data presentation, all reference potentials were converted to RHE using the formula: $E_{\text{RHE}} = E_{\text{measured}} + E_{\text{Ag|AgCl}} + 0.059\text{pH}$. Linear sweep voltammograms (LSVs) were conducted at a scan rate of 5 mV s⁻¹. Galvanostatic stability measurements were performed at a current density of 10 mA cm⁻² for 12 h using a stirrer bar to mitigate mass transfer effects. Electrochemical impedance measurements were carried out at 1.7 V vs. RHE (the potential at which the current density of the CoFe₂O₄ electrode was ~10 mA cm⁻²) in the frequency range 0.01 Hz to 10 kHz with a 10 mV amplitude. To more accurately reflect the behaviour of the CoFe₂O₄ electrocatalyst, an iR correction was applied to all data before analysis ($R = 15 \Omega$ for CoFe₂O₄ and $R = 11 \Omega$ for F:SnO₂) [19].

3. Results and discussion

CoFe₂O₄ thin films were prepared by AACVD at 500 °C as reported elsewhere [19]. Films deposited at this temperature consisted of phase pure CoFe₂O₄ in the bulk with no evidence of common impurity phases such as Co₃O₄ or α -Fe₂O₃ as evident by X-ray diffraction studies [19]. Energy dispersive X-ray spectroscopy, however, revealed that the films had a slight excess of Co on the surface compared to bulk [19]. The typical film consisted of structures of 0.5–1 μm in diameter rising from the surface, giving a film thickness ranging from 1 to 3 μm , depending on the height of individual features [19].

In order to compare the electrocatalytic performance of CoFe₂O₄ against other reported materials from literature, it is important to determine the specific activity of the electrocatalytic material by taking into account the electrochemically active surface area (ECSA) [20]. The ECSA can be calculated from the differential capacitance (C_d) of the material using the following equation; where C_s is the specific capacitance of a smooth and planar electrode measured in the same experimental conditions:

$$\text{ECSA} = \frac{C_d}{C_s}$$

C_d was determined from cyclic voltammograms measured at various scan rates at a potential range where there was no or minimal faradaic activity. C_d was calculated from the following equation, where v is the scan rate and i_c is the charging current:

$$i_c = v C_d$$

The data for the ECSA estimation is shown in Fig. 1. A value of 0.040 mF cm⁻² was used for C_s , which is based on a typical value for a

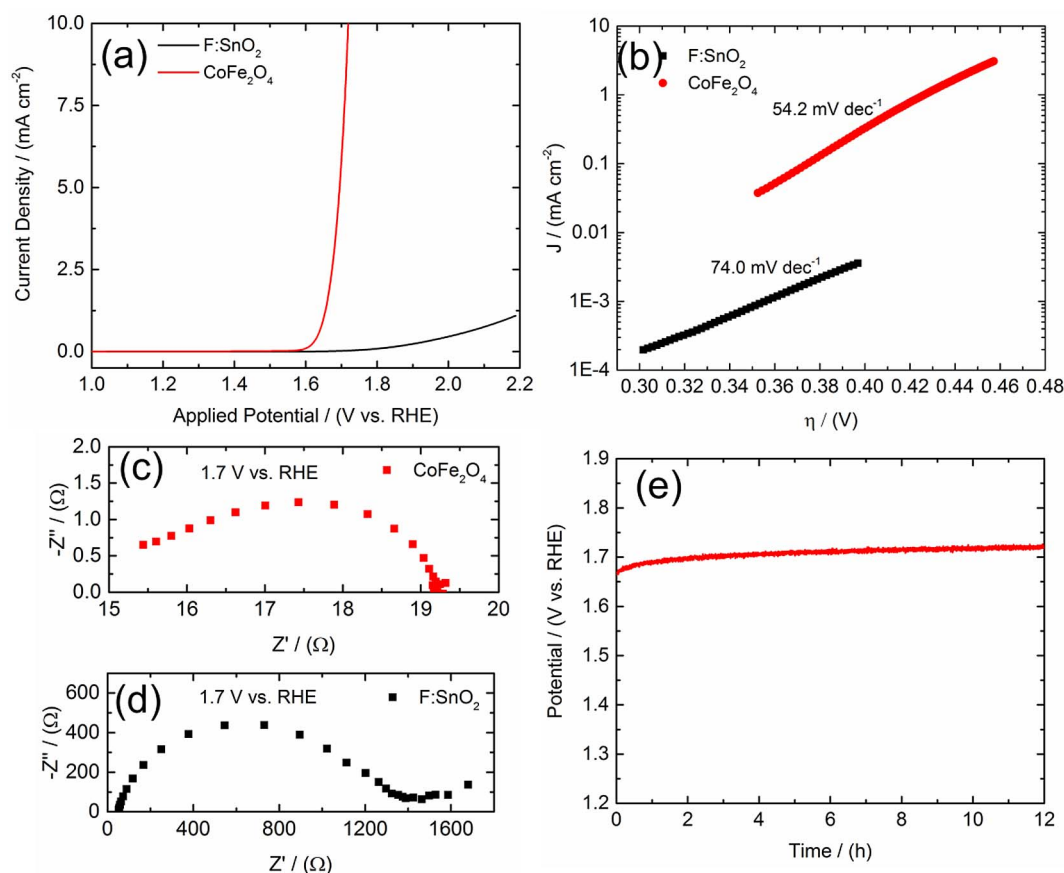


Fig. 2. (a) Linear sweep voltammogram and (b) Tafel plot of CoFe_2O_4 and F:SnO_2 measured at a scan rate of 5 mV s^{-1} in 1 M NaOH . Nyquist plot of (c) CoFe_2O_4 and (d) F:SnO_2 measured at 1.7 V vs. RHE (at which the current density of the CoFe_2O_4 electrode is $\sim 10 \text{ mA cm}^{-2}$) at a frequency range of 10 kHz to 0.01 Hz . (e) Galvanostatic stability measurement of CoFe_2O_4 at a current density of 10 mA cm^{-2} for 12 h .

metal electrode in an aqueous NaOH solution [20]. The ECSA was determined for the F:SnO_2 substrate with and without the CoFe_2O_4 coating for comparison. The ECSA for the F:SnO_2 and CoFe_2O_4 was 0.048 and 5.70 cm^2 , respectively. As the geometric area of the electrodes during the measurement was kept at 1 cm^2 , the roughness factor of the CoFe_2O_4 was 5.70 . The ECSA values are lower than expected, given the highly nanostructured nature of the electrode, and especially as the geometric area of the electrodes was 1 cm^2 . This is likely due to the difficulty of accurately measuring C_s as most films show significant roughness and by the fact that oxides have different specific capacitances than metals [21]. Nevertheless, the values are sufficient to allow comparison between different materials.

The LSVs of the F:SnO_2 and CoFe_2O_4 electrodes are shown in Fig. 2a. The LSV of the F:SnO_2 shows that the substrate has very poor activity towards the OER. The CoFe_2O_4 electrode gives a current density of 10 mA cm^{-2} at 1.72 V vs. RHE , which corresponds to an overpotential of 490 mV . Normalising the current density with respect to the ECSA, the intrinsic activity of CoFe_2O_4 is $1.75 \text{ mA cm}_{\text{real}}^{-2}$ at an overpotential of 490 mV . Tafel analysis was performed on the voltammetry data collected at 5 mV s^{-1} and is shown in Fig. 2b. The Tafel slope of F:SnO_2 and CoFe_2O_4 was found to be 74.0 and 54.2 mV dec^{-1} , respectively. The smaller Tafel slope of CoFe_2O_4 compared with the F:SnO_2 substrate shows the superior electrocatalytic activity of CoFe_2O_4 towards the OER. It is generally understood that a Tafel slope close to 60 mV dec^{-1} is associated with a rate-limiting chemical step following the first electron transfer [5,22]. It appears that the Tafel slope of CoFe_2O_4 might be influenced by a small oxidation peak occurring just before/on the onset of oxygen evolution. This oxidation peak is attributed to the oxidation of CoO_x species on the surface to CoOOH [19]. Fig. 3 shows LSVs for CoFe_2O_4 at different rates of stirring. It can be seen that the

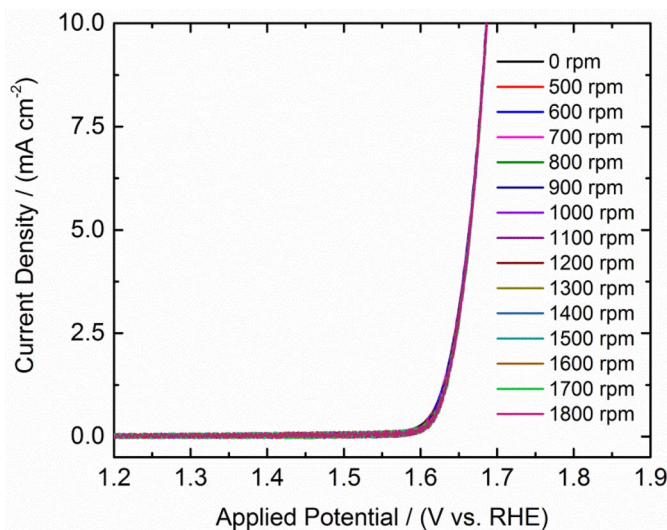


Fig. 3. Linear sweep voltammograms of CoFe_2O_4 at a scan rate of 5 mV s^{-1} in 1 M NaOH measured at various solution stirring rates.

LSVs almost perfectly overlap, showing that the current is independent of the stirring rate; therefore effects from mass transfer can be neglected and the Tafel analysis is valid. Fig. 2c and d show the impedance spectra of CoFe_2O_4 and F:SnO_2 , respectively at 1.7 V vs. RHE , which is the potential at which a current density of 10 mA cm^{-2} was obtained for CoFe_2O_4 . The CoFe_2O_4 electrode shows a charge transfer resistance (R_{ct}) of around 4Ω , compared to F:SnO_2 which shows a R_{ct} of around $1.3 \text{ k}\Omega$. The CoFe_2O_4 demonstrates excellent stability as indicated by

the galvanostatic stability measurement shown in Fig. 2e. A constant current of 10 mA cm^{-2} was applied for 12 h during which the potential only slightly increased from 1.66 V to 1.72 V vs. RHE, a difference of only 0.06 V. X-ray diffraction measurements revealed no changes in the XRD pattern before and after stability measurements, suggesting that the bulk material did not undergo any oxidation during the 12 h stability measurement period. This demonstrates that CoFe_2O_4 is an excellent candidate as a stable OER electrocatalyst in alkaline media. The AACVD CoFe_2O_4 catalyst coatings can be easily made on different substrates providing more flexibility for using it in various device configurations [23].

4. Conclusions

In this work we have shown that CoFe_2O_4 , which is a cheaper alternative to RuO_2 and IrO_2 , has good electrocatalytic activity towards the OER. An overpotential of 490 mV was required to drive a 10 mA cm^{-2} current density. Taking into account the ECSA, CoFe_2O_4 exhibited a very high intrinsic activity of $1.75 \text{ mA cm}_{\text{real}}^{-2}$ at an overpotential of 490 mV. CoFe_2O_4 exhibited excellent stability in alkaline media, retaining catalytic activity for at least 12 h. AACVD is an easily scalable and flexible technique for large-scale catalyst manufacturing. This work shows that very highly electroactive CoFe_2O_4 can be prepared with a higher surface area, for example, on a porous conducting support like carbon nanotubes.

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References

- [1] J. Chow, R.J. Kopp, P.R. Portney, Energy resources and global development, *Science* 302 (2003) 1528–1531, <http://dx.doi.org/10.1126/science.1091939>.
- [2] D.A.J. Rand, R. Dell, *Hydrogen Energy: Challenges and Prospects*, Royal Society of Chemistry, 2008.
- [3] ITM Power, (n.d.), <http://www.itm-power.com/>, Accessed date: 6 October 2017.
- [4] Alkaline Water Ionizer, (n.d.), <http://www.panasonic.com/my/consumer/kitchen-appliances/water-filtration/alkaline-ionizer/tk-7585.html>, Accessed date: 6 October 2017.
- [5] M.S. Burke, M.G. Kast, L. Trotochaud, A.M. Smith, S.W. Boettcher, Cobalt-iron (oxy) hydroxide oxygen evolution electrocatalysts: the role of structure and composition on activity, stability, and mechanism, *J. Am. Chem. Soc.* 137 (2015) 3638–3648, <http://dx.doi.org/10.1021/jacs.5b00281>.
- [6] Y. Lee, J. Suntivich, K.J. May, E.E. Perry, Y. Shao-Horn, Synthesis and activities of rutile IrO_2 and RuO_2 nanoparticles for oxygen evolution in acid and alkaline solutions, *J. Phys. Chem. Lett.* 3 (2012) 399–404, <http://dx.doi.org/10.1021/jz2016507>.
- [7] M.E.G. Lyons, S. Floquet, Mechanism of oxygen reactions at porous oxide electrodes. Part 2—oxygen evolution at RuO_2 , IrO_2 and $\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$ electrodes in aqueous acid and alkaline solution, *Phys. Chem. Chem. Phys.* 13 (2011) 5314–5335, <http://dx.doi.org/10.1039/c0cp02875d>.
- [8] S. Trasatti, Physical electrochemistry of ceramic oxides, *Electrochim. Acta* 36 (1991) 225–241, [http://dx.doi.org/10.1016/0013-4686\(91\)85244-2](http://dx.doi.org/10.1016/0013-4686(91)85244-2).
- [9] M. Bajdich, M. García-Mota, A. Vojvodic, J.K. Nørskov, A.T. Bell, Theoretical investigation of the activity of cobalt oxides for the electrochemical oxidation of water, *J. Am. Chem. Soc.* 135 (2013) 13521–13530, <http://dx.doi.org/10.1021/ja405997s>.
- [10] R.D.L. Smith, M.S. Prévot, R.D. Fagan, S. Trudel, C.P. Berlinguette, Water oxidation catalysis: Electrocatalytic response to metal stoichiometry in amorphous metal oxide films containing iron, cobalt, and nickel, *J. Am. Chem. Soc.* 135 (2013) 11580–11586, <http://dx.doi.org/10.1021/ja403102j>.
- [11] R.D.L. Smith, M.S. Prévot, R.D. Fagan, Z. Zhang, P.A. Sedach, M.K.J. Siu, S. Trudel, C.P. Berlinguette, Photochemical route for accessing amorphous metal oxide materials for water oxidation catalysis, *Science* 340 (2013) 60–63, <http://dx.doi.org/10.1126/science.1233638>.
- [12] J. Tian, H. Li, A.M. Asiri, A.O. Al-Youbi, X. Sun, Photoassisted preparation of cobalt phosphate/graphene oxide composites: a novel oxygen-evolving catalyst with high efficiency, *Small* 9 (2013) 2709–2714, <http://dx.doi.org/10.1002/smll.201203202>.
- [13] J. Yano, J. Kern, K. Sauer, M.J. Latimer, Y. Pushkar, J. Biesiadka, B. Loll, W. Saenger, J. Messinger, A. Zouni, V.K. Yachandra, Where water is oxidized to dioxygen: structure of the photosynthetic Mn_4Ca cluster, *Science* 314 (2006) 821–825, <http://dx.doi.org/10.1126/science.1128186>.
- [14] J. Suntivich, K.J. May, H.A. Gasteiger, J.B. Goodenough, Y. Shao-Horn, Perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles, *Science* 334 (2011) 1383–1385.
- [15] R. Subbaraman, D. Tripkovic, K.-C. Chang, D. Strmcnik, A.P. Paulikas, P. Hirunsit, M. Chan, J. Greeley, V. Stamenkovic, N.M. Markovic, Trends in activity for the water electrolyser reactions on 3d $\text{M}(\text{Ni}, \text{Co}, \text{Fe}, \text{Mn})$ hydr(oxy)oxide catalysts, *Nat. Mater.* 11 (2012) 550–557, <http://dx.doi.org/10.1038/nmat3313>.
- [16] A.A. Tahir, K.G.U. Wijayantha, S. Saremi-Yarahmadi, M. Mazhar, V. McKee, Nanostructured $\alpha\text{-Fe}_2\text{O}_3$ thin films for photoelectrochemical hydrogen generation, *Chem. Mater.* 21 (2009) 3763–3772, <http://dx.doi.org/10.1021/cm803510v>.
- [17] Q. Liu, A.M. Asiri, X. Sun, Hematite nanorods array on carbon cloth as an efficient 3D oxygen evolution anode, *Electrochem. Commun.* 49 (2014) 21–24, <http://dx.doi.org/10.1016/j.elecom.2014.09.021>.
- [18] S. Anantharaj, S.R. Ede, K. Sakthikumar, K. Karthick, S. Mishra, S. Kundu, Recent Trends and perspectives in electrochemical water splitting with an emphasis on sulfide, selenide, and phosphide catalysts of Fe, Co, and Ni: a review, *ACS Catal.* 6 (2016) 8069–8097, <http://dx.doi.org/10.1021/acscatal.6b02479>.
- [19] J.S. Sagu, K.G.U. Wijayantha, A.A. Tahir, The pseudocapacitive nature of CoFe_2O_4 thin films, *Electrochim. Acta* 246 (2017) 870–878, <http://dx.doi.org/10.1016/j.electacta.2017.06.110>.
- [20] C.C.L. McCrory, S. Jung, J.C. Peters, T.F. Jaramillo, Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction, *J. Am. Chem. Soc.* 135 (2013) 16977–16987, <http://dx.doi.org/10.1021/ja407115p>.
- [21] M. Kölbach, S. Fiechter, R. van de Krol, P. Bogdanoff, Evaluation of electrodeposited $\alpha\text{-Mn}_2\text{O}_3$ as a catalyst for the oxygen evolution reaction, *Catal. Today* 290 (2017) 2–9, <http://dx.doi.org/10.1016/j.cattod.2017.03.030>.
- [22] D.K. Bediako, C. Costentin, E.C. Jones, D.G. Nocera, J.-M. Savéant, Proton–electron transport and transfer in electrocatalytic films. Application to a cobalt-based O_2 -evolution catalyst, *J. Am. Chem. Soc.* 135 (2013) 10492–10502, <http://dx.doi.org/10.1021/ja403656w>.
- [23] P. Marchand, I.A. Hassan, I.P. Parkin, C.J. Carmalt, Aerosol-assisted delivery of precursors for chemical vapour deposition: expanding the scope of CVD for materials fabrication, *Dalton Trans.* 42 (2013) 9406–9422, <http://dx.doi.org/10.1039/c3dt50607j>.