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Electrocatalytic activity of CoFe$_2$O$_4$ thin films prepared by AACVD towards the oxygen evolution reaction in alkaline media

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ABSTRACT

The electrocatalytic behaviour of CoFe$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ was found to be 1.75 mA cm$_{real}^{-2}$ at an overpotential of 490 mV. The CoFe$_2$O$_4$ 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 electrolysers 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 electrolysers 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 (α-Fe$_2$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$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ 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 at the conducting substrate (TEC 8 NSG, 8 Ω/□), which was cut in to
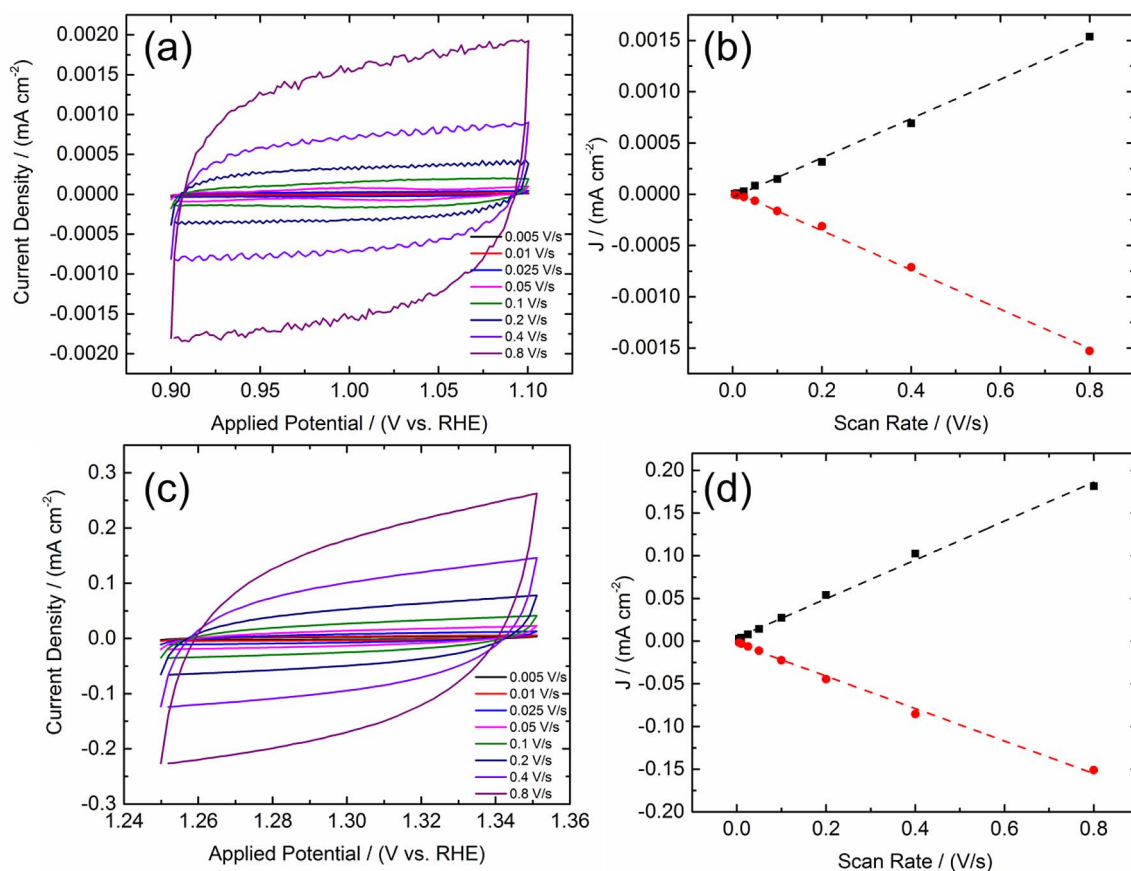

Fig. 1. Determination of differential capacitance of CoFe$_2$O$_4$ and the substrate (F:SnO$_2$) from cyclic voltammetry measurements as a function of scan rate in 1 M NaOH. Cyclic voltammograms of (a) F:SnO$_2$ and (c) CoFe$_2$O$_4$ between scan rates of 5 mV s^{-1}–0.8 V s^{-1}. Anodic and cathodic current density vs. scan rate for (b) F:SnO$_2$ and (d) CoFe$_2$O$_4$ 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 to 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: $E_{RHE} = E_{measured} + E_{Ag|AgCl} + 0.059pH$. 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 CoFe$_2$O$_4$ 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 CoFe$_2$O$_4$ electrocatalyst, an iR correction was applied to all data before analysis (R = 15 Ω for CoFe$_2$O$_4$ and R = 11 Ω for F:SnO$_2$) [19].

3. Results and discussion

CoFe$_2$O$_4$ thin films were prepared by AACVD at 500 °C as reported elsewhere [19]. Films deposited at this temperature consisted of phase pure CoFe$_2$O$_4$ in the bulk with no evidence of common impurity phases such as Co$_3$O$_4$ or α-Fe$_2$O$_3$ 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 CoFe$_2$O$_4$ 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:

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

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
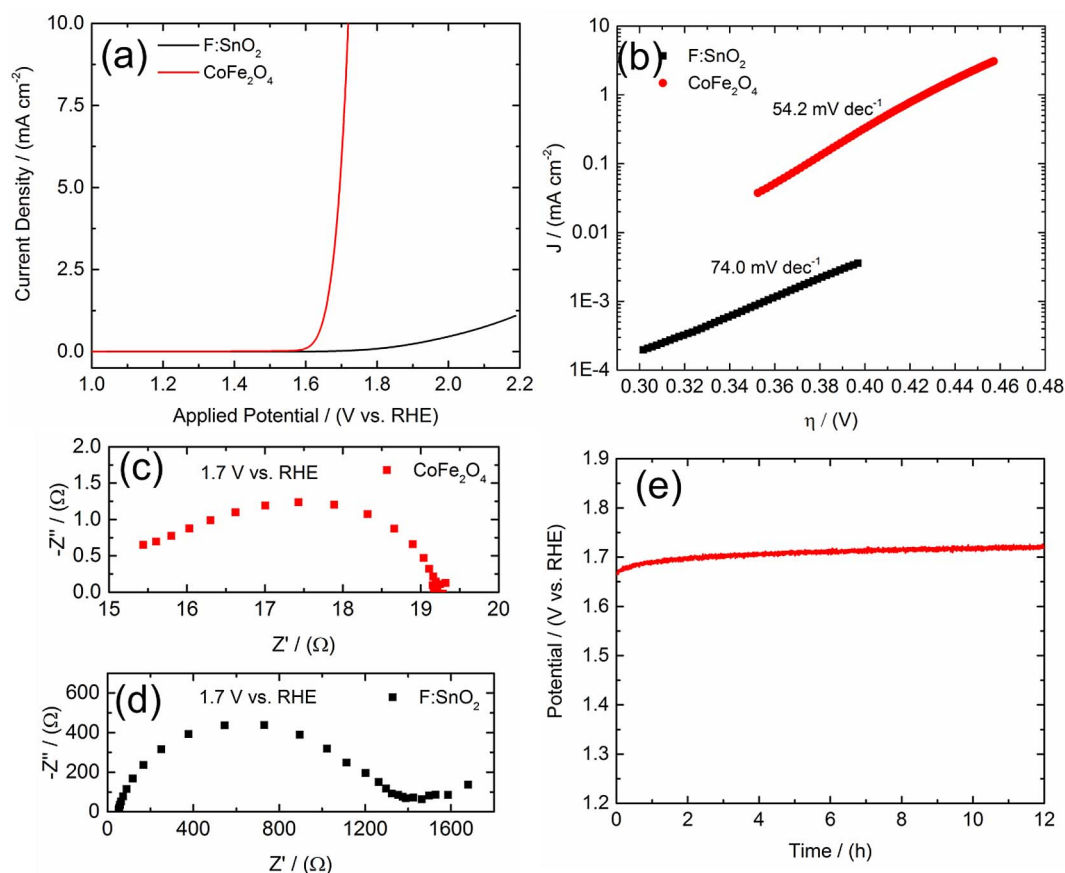
Fig. 2. (a) Linear sweep voltammogram and (b) Tafel plot of CoFe$_2$O$_4$ and F:SnO$_2$ measured at a scan rate of 5 mV s^{-1} in 1 M NaOH. Nyquist plot of (c) CoFe$_2$O$_4$ and (d) F:SnO$_2$ measured at 1.7 V vs. RHE (at which the current density of the CoFe$_2$O$_4$ electrode is ∼10 mA cm^{-2}) at a frequency range of 10 kHz to 0.01 Hz. (e) Galvanostatic stability measurement of CoFe$_2$O$_4$ 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$_2$O$_4$ coating for comparison. The ECSA for the F:SnO$_2$ and CoFe$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ is 1.75 mA cm$_{real}^{-2}$ 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$_2$O$_4$ was found to be 74.0 and 54.2 mV dec^{-1}, respectively. The smaller Tafel slope of CoFe$_2$O$_4$ compared with the F:SnO$_2$ substrate shows the superior electrocatalytic activity of CoFe$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ at different rates of stirring. It can be seen that the
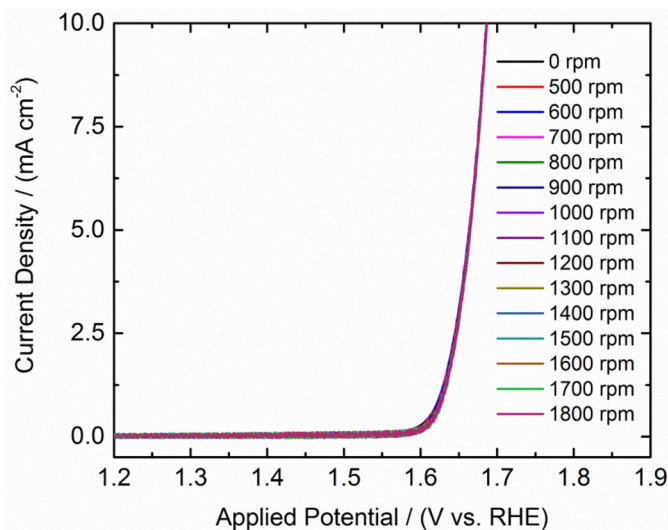

Fig. 3. Linear sweep voltammograms of CoFe$_2$O$_4$ at a scan rate of 5 mV s^{-1} in 1 M NaOH measured at various solution stirring rates.

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$_2$O$_4$ 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$_2$O$_4$. The CoFe$_2$O$_4$ electrode shows a charge transfer resistance (R_{ct}) of around 4 Ω, compared to F:SnO$_2$ which shows a R_{ct} of around 1.3 kΩ. The CoFe$_2$O$_4$ 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 mA cm$_{real}^{-2}$ 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.

Acknowledgements

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