Electrochemistry Communications 87 (2018) 1–4

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

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

Jagdeep S. Sagu, Diana Mehta, K.G. Upul Wijayantha*

*Energy Research Laboratory (ERL), Department of Chemistry, Loughborough University, Loughborough, LE11 3TU, UK*

ARTICLE INFO

*Keywords:*
Thin film
Electrocatalyst
OER
AACVD
Oxide
Alkaline

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 mA $cm^{-2}_{real}$ 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 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 ($\alpha$-$Fe_2O_3$) 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 Ω/□), which was cut in to

* Corresponding author.
*E-mail address:* U.Wijayantha@lboro.ac.uk (K.G.U. Wijayantha).

https://doi.org/10.1016/j.elecom.2017.12.017
Received 9 October 2017; Received in revised form 4 December 2017; Accepted 14 December 2017
Available online 15 December 2017

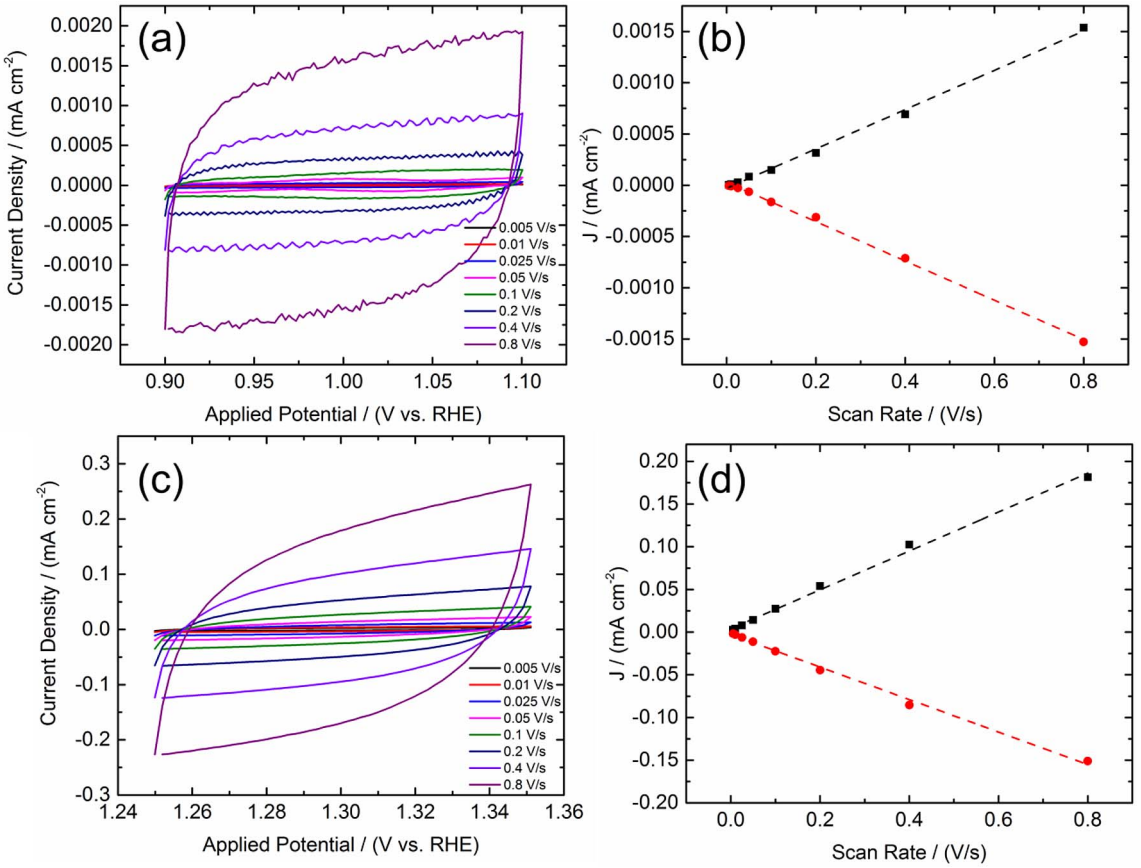


**Fig. 1.** Determination of differential capacitance of $CoFe_2O_4$ and the substrate (F:$SnO_2$) from cyclic voltammetry measurements as a function of scan rate in 1 M NaOH. Cyclic voltammograms of (a) F:$SnO_2$ and (c) $CoFe_2O_4$ between scan rates of 5 mV $s^{-1}$–0.8 V $s^{-1}$. Anodic and cathodic current density vs. scan rate for (b) F:$SnO_2$ and (d) $CoFe_2O_4$ 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 $CoFe_2O_4$ 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 $CoFe_2O_4$ electrocatalyst, an iR correction was applied to all data before analysis ($R$ = 15 Ω for $CoFe_2O_4$ and $R$ = 11 Ω for F:$SnO_2$) [19].

## 3. Results and discussion

$CoFe_2O_4$ thin films were prepared by AACVD at 500 °C as reported elsewhere [19]. Films deposited at this temperature consisted of phase pure $CoFe_2O_4$ in the bulk with no evidence of common impurity phases such as $Co_3O_4$ or α-$Fe_2O_3$ 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 $CoFe_2O_4$ 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:

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

$C_d$ 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 $\upsilon$ is the scan rate and $i_c$ is the charging current:

$$i_c = \upsilon\, C_d$$

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