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作品編號　**030008**

參展科別　化學

作品名稱　**Electrodeposited Co-Based Alloys as Bifunctional Electrocatalysts for Overall Water Splitting**

就讀學校　國立科學工業園區實驗高級中學

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關鍵詞　**Electrocatalysis、Hydrogen Production、Electrodeposition**

作者簡介

我是朱翊，就讀竹科實中。很開心透過這次機會認識科學研究，使原先對研究有些排斥的我大為改觀。感謝教授及學長姐們的提攜，教導我該領域的相關知識及做實驗的方法，指引我前往正確的方向。在一次次的實驗中，經歷過徬徨迷惘、苦惱，當然也有歡笑與驚喜，在不斷地修正、調整之下，終於使研究更臻完備。這場旅程，每一刻皆是我成長的養分。

摘要

人們對能源的大量需求，導致全球暖化與資源耗盡。本研究開發出新型水電解觸媒，以提升水裂解時產氫與產氧的效能。目前市面上所用的金屬觸媒如鉑、鈀，數量稀少且價格高昂，造成氫能發展受到限制。因此選用價格相對便宜的鈷作為核心製作水電解觸媒，比較單金屬與雙金屬觸媒的效能差異，以尋求效能最佳的觸媒。接著，針對各樣本進行多項分析，包括線掃描伏安法、X 射線繞射儀掃描鑑定、穿隧式電子顯微鏡等。使用電鍍法則是因為其過程簡便快速，且能有效合成穩定、均勻的結構與表面型態，具大量生產、商業化的潛力。由結果可知，鈷鉬合金觸媒活性表現最佳，行析氧反應(OER)時，有相當低的過電位(η = 290 mV@10 mA cm^{-2})及塔弗斜率（61.1 mV/dec)；行析氫反應(HER)時，其過電位(η = 56.8 mV@10 mA cm^{-2})和塔弗斜率（93.6 mV/dec)亦有良好表現。期望未來能將研究成果應用於綠色能源與工業中，解決現今面臨的能源危機。

Abstract

Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) provide an attractive path to obtain sustainable energy and tackle the issue of global warming. However, today HER and OER highly depend on noble-metal-based catalysts such as Pt and Ru, which obstructs the large-scale commercial applications of energy conversion devices. In this study, the Co-based electrocatalysts were prepared by electrodeposition. Electrodeposition method is a simple and fast technology to construct multi-composition materials. By adjusting ratio of metals and reaction time, we successfully synthesized Co, Co-Mo and Co-W catalysts respectively. The better catalyst can be obtained under the kinetics conditions of 65℃ and 1 hour. After coated onto the Nickel foam, the electrocatalysts were examined by scanning electron microscope (SEM) and X-ray diffractometer (XRD). Among three different catalysts, Co-Mo shows the highest efficiency for catalyzing OER at low overpotential (η = 290 mV@10 mA cm^{-2}), and the tafel slope is 61.1 mV/dec. In the meantime, it also shows the highest efficiency for catalyzing HER at low overpotential (η = 56.8 mV@10 mA cm^{-2}), and the tafel slope is 93.6 mV/dec. The outstanding performance enlists these electrocatalysts to be promising candidates as low-cost anode and cathode materials for wide applications in water splitting.

1. Introduction

1.1 Purpose of the Research

Ir and Ru-based nanoparticles appear as the most efficient OER electrocatalysts in recent decades. However, the scarcity and poor stability remain the huge barriers to the implementation of these precious metals in practical hydrogen production. Therefore, the exploration of high-efficiency and cost-effective OER electrocatalysts is of great significance for the large-scale production and application of hydrogen energy in renewable energy technology fields.

To verify the synergistic effect, this study synthesized Co and Co-based electrocatalysts (Co-W, Co-Mo) and compared their HER and OER performances. Co and Co-based electrocatalysts were produced by electrodeposition process which offers important advantages and unique possibilities in the development of nanostructure. Using this technique, it is possible to obtain a metal nanocoating in a single step process. Co and Co-based electrocatalysts were examined by various methods, such as linear sweep voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Their morphologies were also confirmed by scanning electron microscope (SEM) and X-ray diffractometer (XRD). Additionally, this study adjusted Co/W molar ratio and Co/Mo molar ratio to obtain the optimized electrocatalysts.

2. Method and Procedure

2.1 Fundamental of HER and OER

Fundamentals of HER and OER electrochemical water splitting can produce pure hydrogen at the cathode and oxygen at the anode in an electrolytic cell, which are two very critical half-cell reactions for electrochemical water-electrolysis. The water splitting reaction can be expressed as follows:

$$2H_2O \rightarrow 2H_2 + O_2$$

The reactions at the cathode and anode parts for the water-splitting reaction under alkaline condition can be expressed as follows:

Cathode reaction:

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \quad E^0 = -0.83V$$

Anode reaction:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad E^0 = -0.40V$$

The thermodynamic voltage of water splitting is 1.23 V (vs normal hydrogen electrode (NHE)) at 25℃ and 1 atm, but much higher potentials are needed to drive efficient water splitting. This excess potential, which is called the overpotential (η), is required to overcome the intrinsic activation barriers during the electrode reaction. The actual applied potential for the two half-cell reactions of water splitting can be expressed as follows:

$$E_{HER} = E^0_{HER} + iR + \eta_{HER}$$

$$E_{OER} = E^0_{OER} + iR + \eta_{OER}$$

iR is the ohmic potential drop of the system and η is the overpotential, $E^0_{HER} = 0$ and $E^0_{OER} = 1.23$ V. In this study, iR compensation is 95%.

2.2 Hydrogen Evolution Reaction (HER)

HER is a two-electron transfer process that occurs on the cathode in water electrolysis. In general, this multi-step elementary reaction mechanism is called the Volmer-Heyrovsky mechanism or the Volmer-Tafel mechanism as illustrated as follows:

For Volmer-Heyrovsky mechanism in alkaline condition:

$$H_2O_{(l)} + e^- + * \rightarrow H^* + OH^-(aq), \text{ Volmer reaction}$$

$$H^* + H_2O_{(l)} + e^- \rightarrow H_{2(g)} + OH^-_{(aq)} + *, \text{ Heyrovsky reaction}$$

For Volmer-Tafel mechanism in alkaline condition:

$$H_2O_{(l)} + e^- + * \rightarrow H^* + OH^-_{(aq)}, \text{ Volmer reaction}$$

$$H^* + H^* \rightarrow H_{2(g)} + 2*, \text{ Tafel reaction (acidic and alkaline)}$$

* denotes an empty active site, and H* denotes a hydrogen atom bonded to the active site.

2.3 Oxygen Evolution Reaction (OER)

Oxygen evolution reaction (OER) is a four-electron transfer process with a very sluggish reaction rate that severely limits oxygen production, thus, the reaction process of OER is relatively complicated. They are basically discussed around three intermediates (O*, OH*, and OOH*). Currently, the generally recognized reaction mechanisms of OER can be illustrated as follows: Proposed mechanism under alkaline conditions:

$$M + OH^- \rightarrow MOH$$

$$MOH + OH^- \rightarrow MO + H_2O_{(l)}$$

$$2MO \rightarrow 2M + O_{2(g)}$$

$$MO + OH^- \rightarrow MOOH + e^-$$

$$MOOH + OH^- \rightarrow M + O_{2(g)} + H_2O$$

2.4 Preparation of Co, Co-Mo and Co-W Electrodes

The three electrodes have been produced by electrodeposition on Nickel foam (NF). The principle of the electrodeposition is shown in Fig. 1. First, the reactants are dissolved in the electrolyte. By fine-tuning the applied cell potential, the oxidizing or reducing products can be continuously deposited on the surface of the working electrode (WE) or counter electrode (CE). All electrodeposition, lasting 1 hour, have been carried out at 5V and 65°C.

Reagents	Co	Co-Mo	Co-W
$Na_3C_6H_5O_7$	0.5M	0.5M	0.5M
$CoN_2O_6 \cdot 6H_2O$	0.23M	0.23M	0.23M
Na_2MoO_4	-	0.08M/0.23M/0.69M	-
$Na_2WO_4 \cdot 2H_2O$	-	-	0.08M/0.23M/0.69M

Table 1 Composition of the three used electrolytes

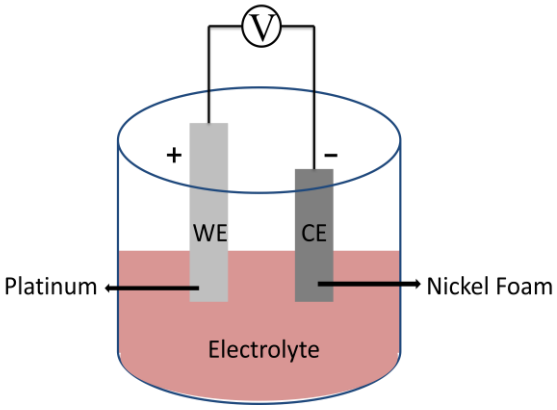

Fig. 1 Principle of the electrodeposition

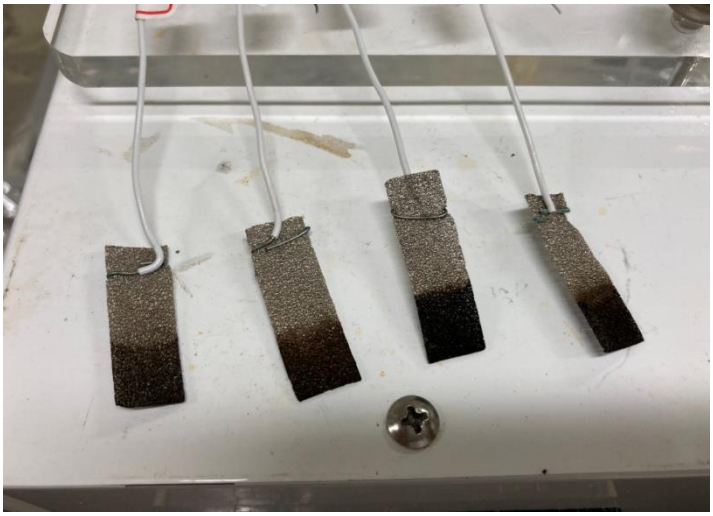

Fig. 2 Co-W electrodeposited on nickel foam

3. Results and Discussion

3.1 Electrochemical Measurement

Electrochemical measurements were performed in a electrochemical workstation (CH Instruments) in a typical three-electrode setup. An Ag/AgCl (3 M KCL) electrode and a platinum electrode were used as the reference and counter electrode, respectively. In this study, $E_{RHE} = E + E_{Ag/AgCl} + 0.059*14(\text{pH value}) = E + 1.023$

Linear sweep voltammetry (LSV) is a method where there is linear variation of the electrode potential with time with the scan rate (v). In LSV, only the first half-cycle of a cyclic voltammogram is executed. Scanning starts at a potential where no electrochemical reaction occurs. Current can be observed at the potential where the charge transfer begins, which increases with the potential. In this project, LSV were carried out with scan rate 20 mV s^{-1} over a range from -0.9 to +1.3 V for HER and 0 to 0.7 V for OER. All the experiments were carried out at room temperature in 1M KOH solutions.

3.2 Results of HER

3.2.1 Overpotential and Tafel Slope

In Fig. 3, it shows that the overpotential of Co is 150 mV at 10 mA cm^{-2}, and the tafel slope is 149 mV/dec.

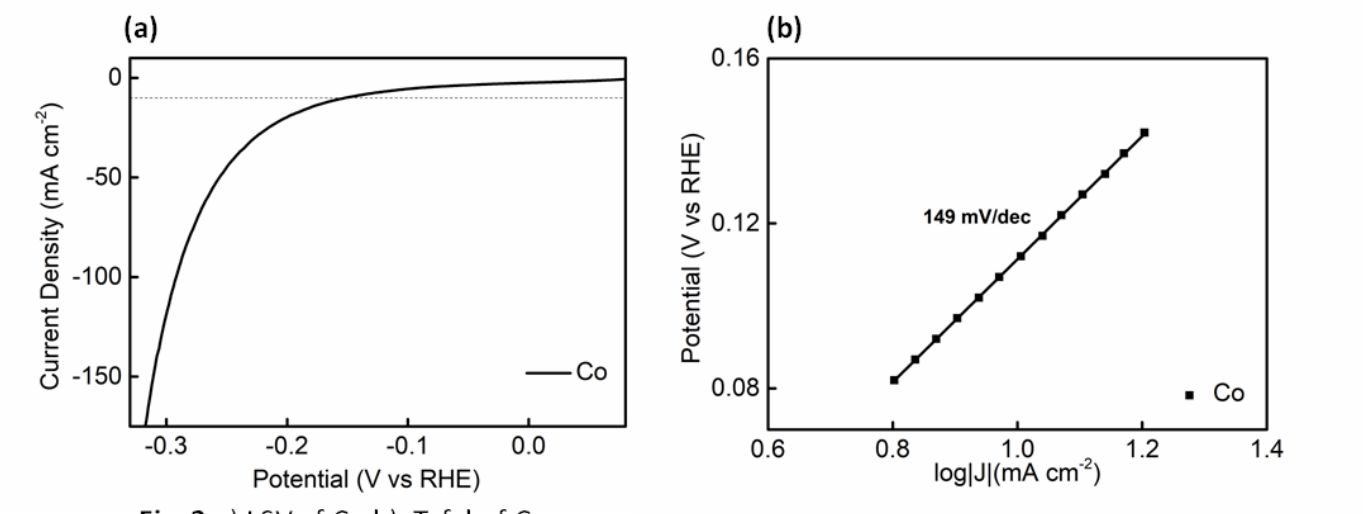

Fig. 3 a) LSV of Co b) Tafel of Co

Among three different Co-Mo electrodes as illustrated in Fig. 4, the highest electrocatalytic activity exhibits at a Co/Mo molar ratio of 1:1, whose overpotential is 56.8 mV at 10 mA cm^{-2}, and the tafel slope is 93.6 mV/dec.

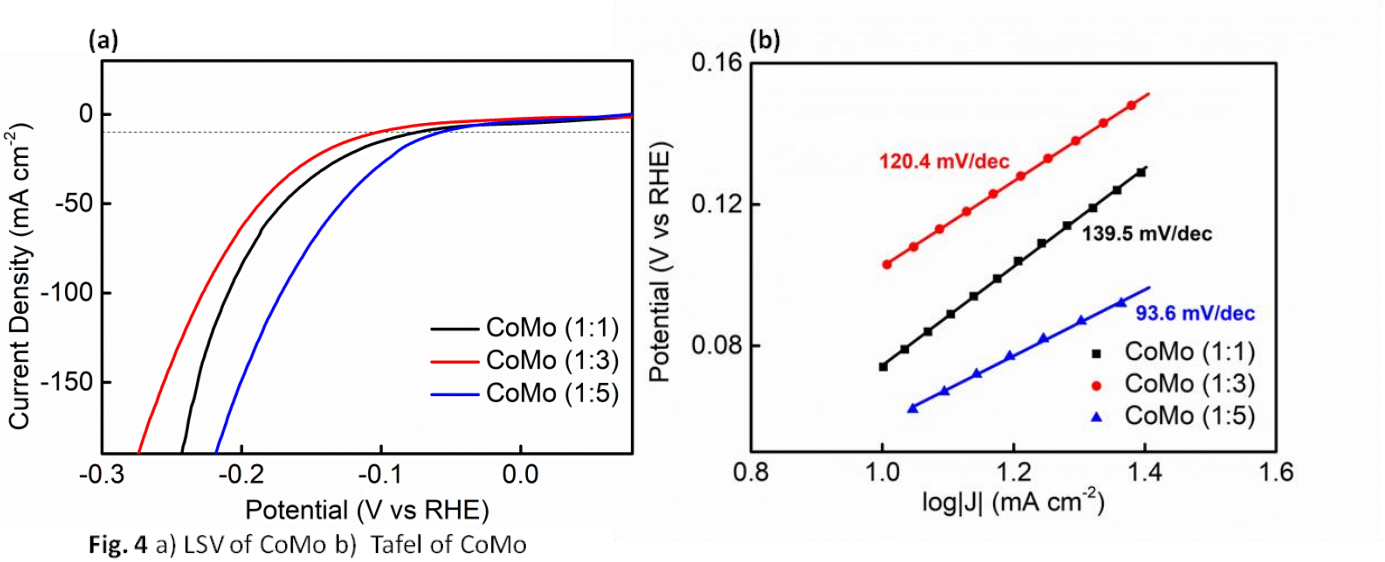

Fig. 4 a) LSV of CoMo b) Tafel of CoMo

On the other hand, among three different Co-W electrodes as illustrated in Fig. 5, the lowest overpotential exhibits at a Co/W molar ratio of 1:1, whose overpotential is 135 mV at 10 mA cm^{-2}. The lowest tafel slope exhibits at a Co/W molar ratio of 1:3, whose tafel slope is 84.0 mV/dec.

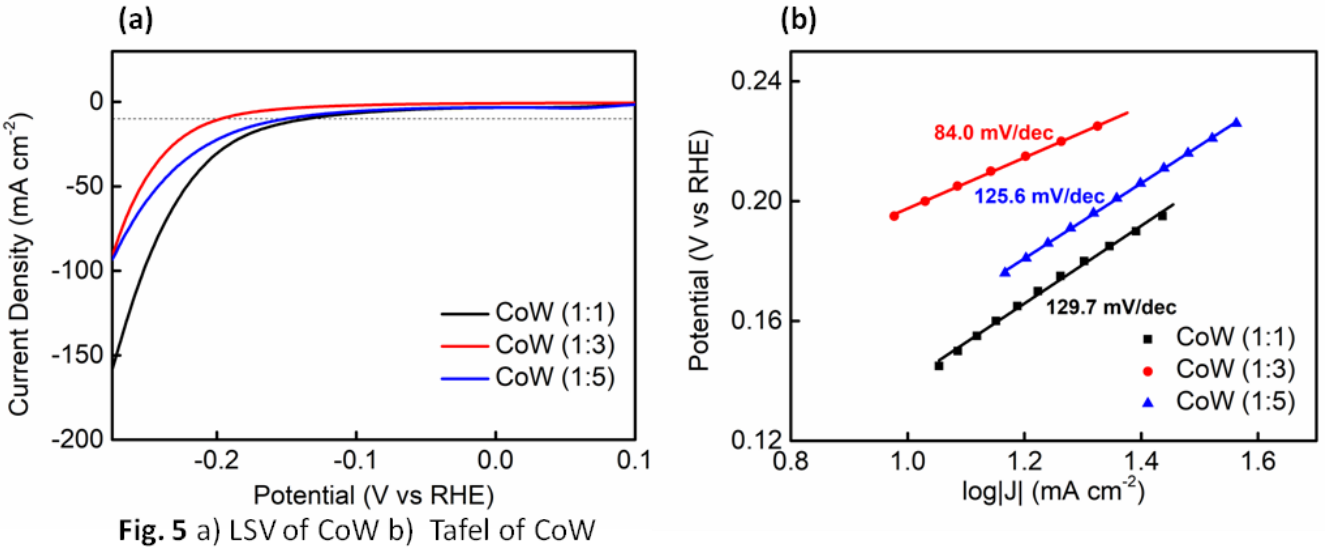

Fig. 5 a) LSV of CoW b) Tafel of CoW

3.2.2 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopic (EIS) is an electrochemical techniques to measure the impedance of a system in dependence of the AC potentials frequency. In this study, EIS measurements were carried out in 1 M KOH at different potentials in the frequency range 10^{-1} to 10^{6} Hz. The Nyquist plots of Co-Mo and Co-W for the hydrogen evolution reaction are shown in Fig. 6 below. The radius of semicircle refers to charge transfer resistance (R_{ct}), and the smaller R_{ct} results better electrochemical behaviour. That is, the impact of Co/Mo ratio on R_{ct} is trivial, each of them has similar radius. However, the Co/W molar ratio of 1:1 has the smallest R_{ct} among 6 electrocatalysts. In the meantime, it has the lowest overpotential among 3 Co-W electrocatalysts,

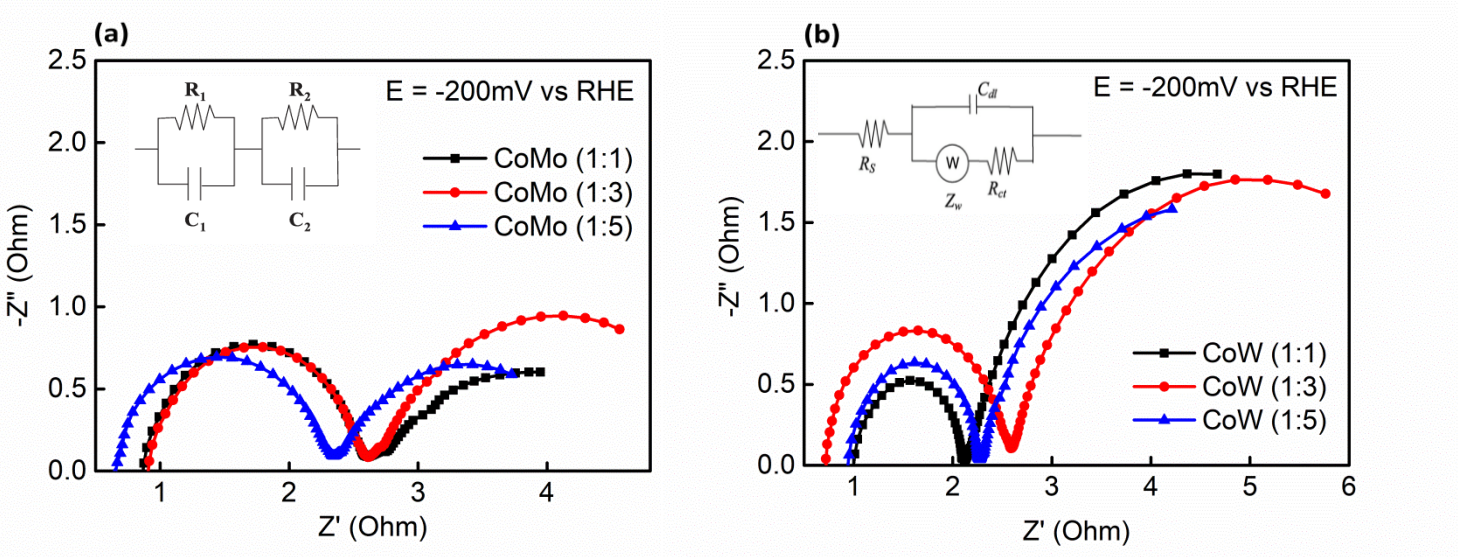

Fig. 6 a) the Nyquist plot of CoMo b) the Nyquist plot of CoW. The equivalent circuit is shown on the upper-left side of the plot. C_{dl} represents double layer capacitance, Z_w represents the Warburg impedance, and R_s represents solution resistance.

3.3 Results of OER

1) Overpotential and Tafel Slope

In Fig. 7, the overpotential of Co for OER is 330 mV, and the tafel slope is 79.4 mV/dec.

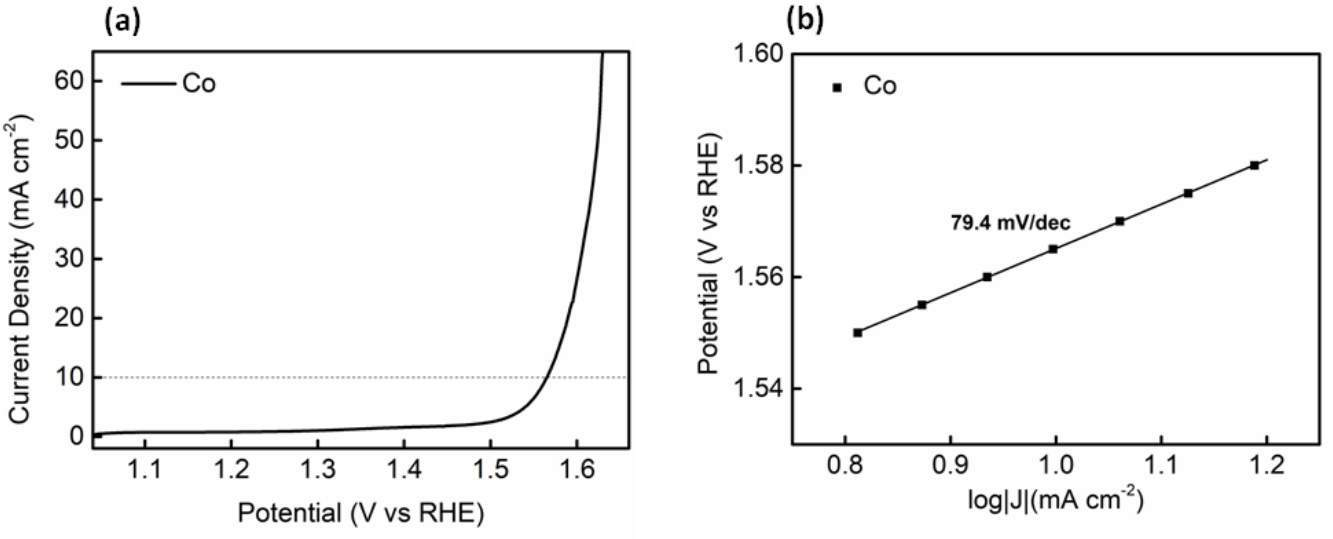

Fig. 7 a) LSV of Co b) Tafel of Co

In Fig. 8, overpotentials of Co-Mo (1:1), Co-Mo (1:3), Co-Mo (1:5) are 290 mV, 294 mV and 320 mV respectively. Notably, the Co/Mo molar ratio of 1:1 has both lowest overpotential and lowest tafel slope (61.1 mV/dec), which indicates its high efficiency.

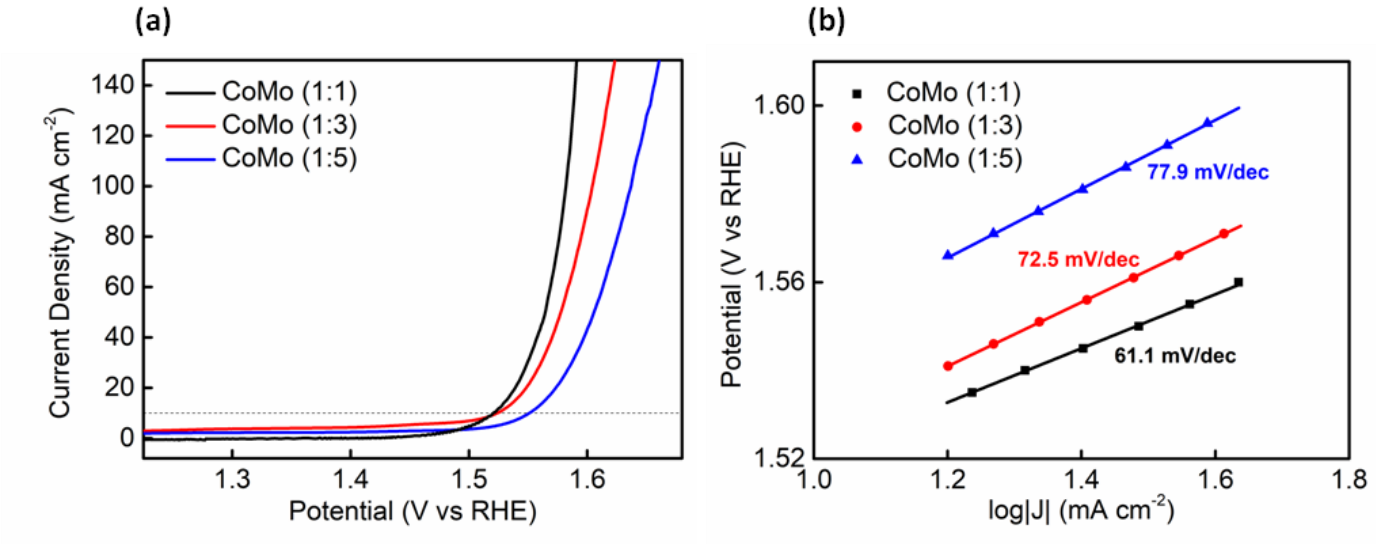

Fig. 8 a) LSV of CoMo b) Tafel of CoMo

In Fig. 9, overpotentials of Co-W (1:1), Co-W (1:3), Co-W (1:5) are 308 mV, 301 mV and 299 mV respectively. Among three Co-W catalysts of different Co/W ratio, Co-W (1:5) exhibits the best performance, which has low overpotential (299 mV@10 mA cm^{-2}) and low tafel slope (69.8 mV/dec).

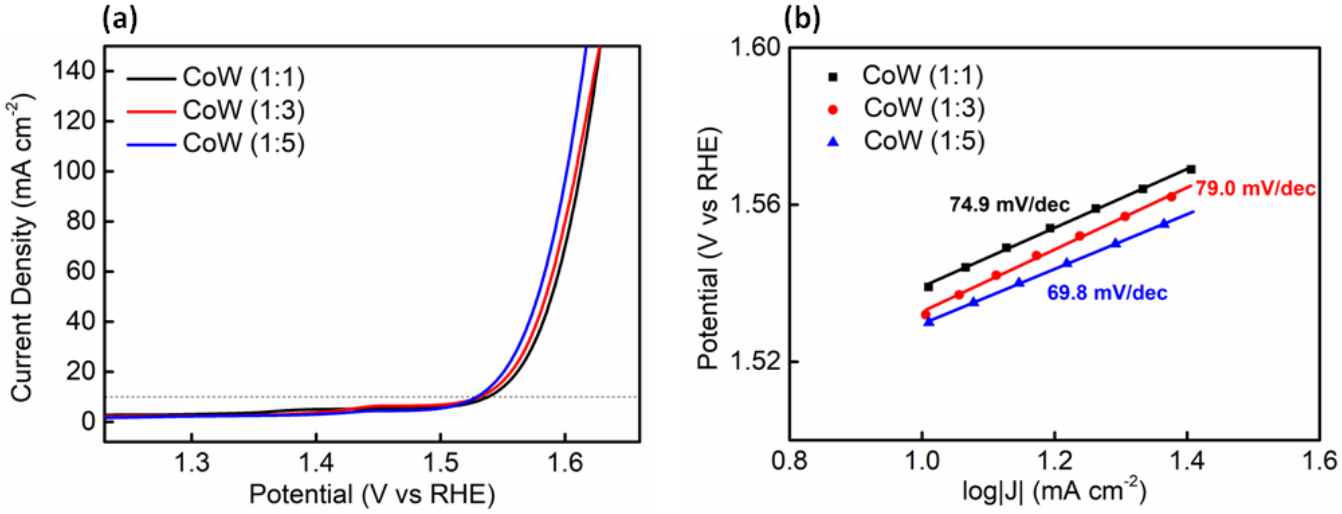

Fig. 9 a) LSV of CoW b) Tafel of CoW

2) Electrochemical Impedance Spectroscopy

Fig. 10 (a) shows the Nyquist plot of Co-Mo for HER. It has the similar result as the Nyquist plot of Co-Mo for OER. Three radiuses of semicircles on the Nyquist plot are close to each other. On the other hand, Co-W catalysts of different Co/W ratio have distinct radiuses. Additionally, Co-W (1:5), which shows the highest efficiency among three Co-W catalysts, has the smallest R_{ct}. This proves the correlation between R_{ct} and efficiency of catalysts.

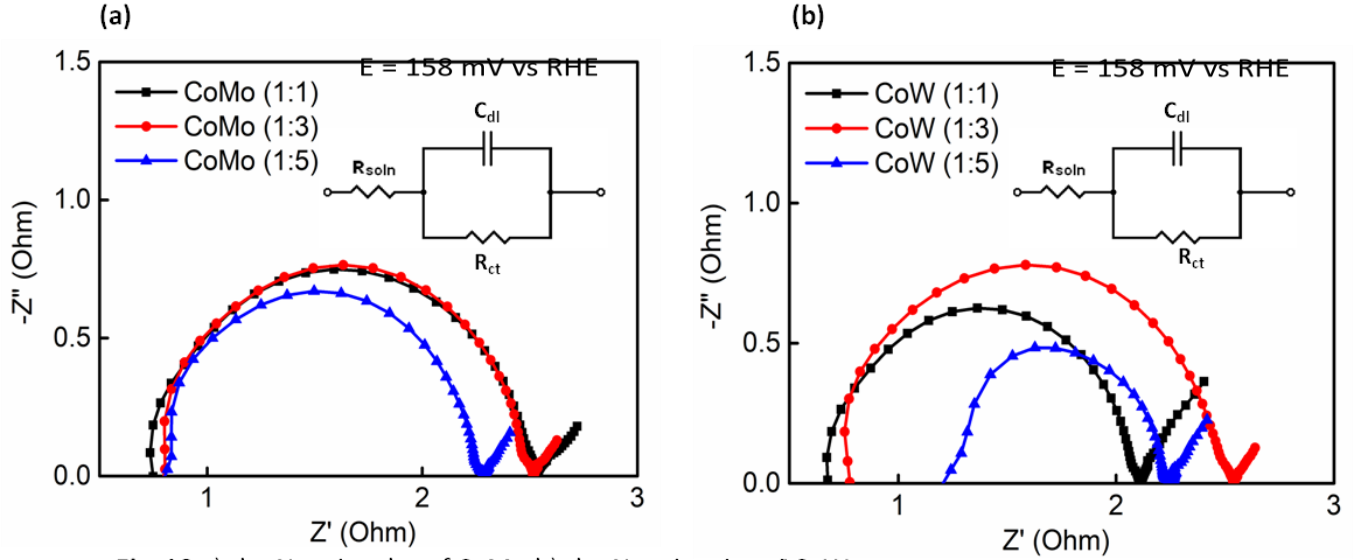

Fig. 10 a) the Nyquist plot of CoMo b) the Nyquist plot of CoW.

3.4 Electrochemical Surface Area (ECSA)

Accurately quantifying ECSA is important for determining catalyst activity, since morphology-dependant OER predominantly occurs at the active surface. The ECSA is estimated from the double layer capacitance (C_{dl}) via cyclic voltammetry (CV) measurement, and it was calculated according to the equation $ECSA=C_{dl}/C_s$.

In Fig. 11, the CV curves in a non-faradaic region were plotted as a function of various scan rates (20, 40, 60, 80, 100 mV/s). Then, the double layer capacitance (C_{dl}) was assessed from the slope of the linear regression between the current density differences in the middle of the potential window of CV curves versus the scan rates. C_s stands for the specific capacitance of standard electrode materials on a unit surface area. In Fig. 11 (d), Co-Mo (1:3) has the largest slope, which indicates that it has larger ECSA than Co-Mo (1:1) and Co-Mo (1:5).

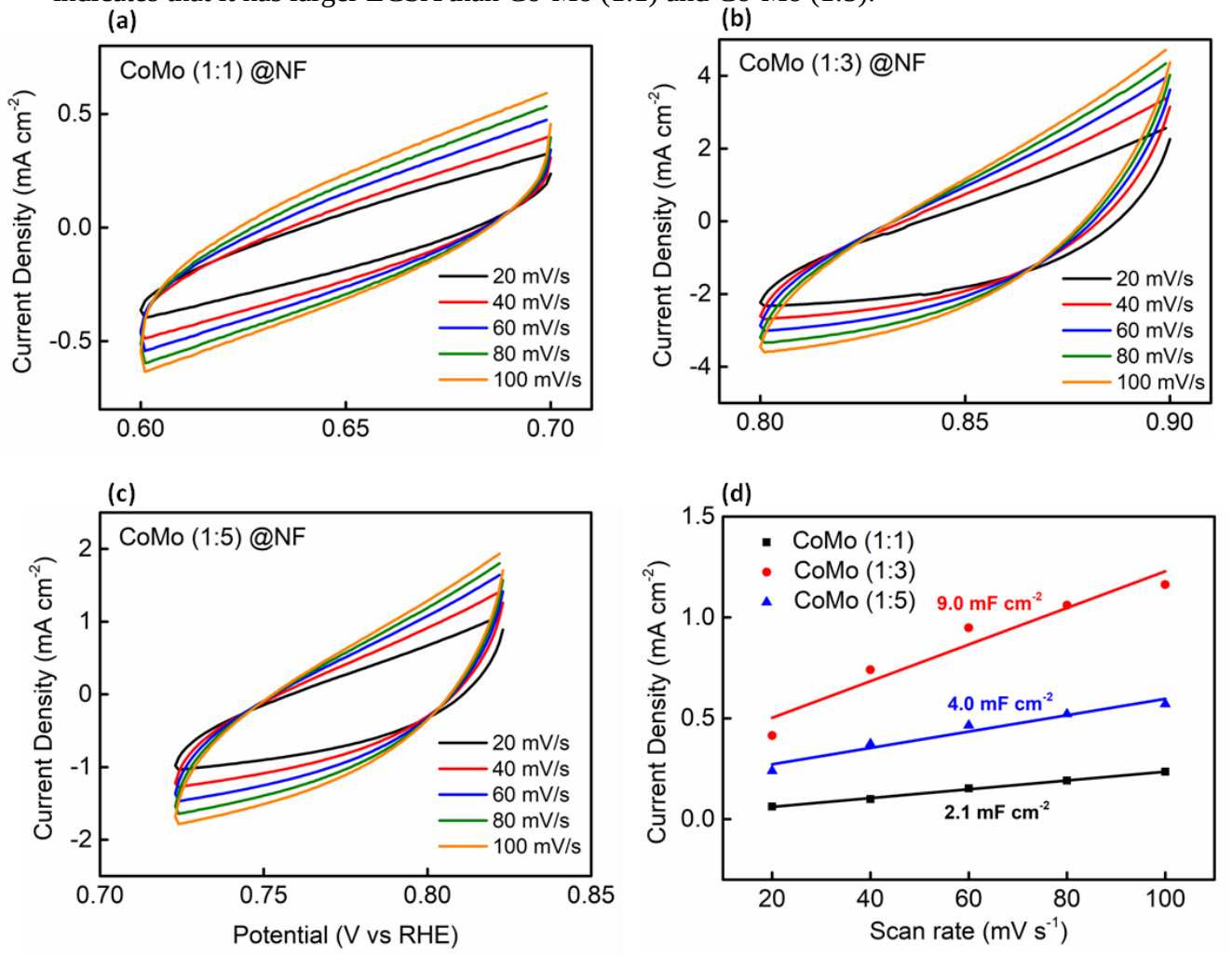

Fig. 11 a) CV of CoMo (1:1) b) CV of CoMo (1:3) c) CV of CoMo (1:5) d) linear regression between the current density differences in the middle of the potential window of CV vs. scan rates for three CoMo samples

In Fig. 12 (d), Co-W (1:1) has the largest slope, which is 12.4 mF cm^{-2}. Meanwhile, Co-W (1:1) has the best efficiency for HER among three Co-W catalysts (The overpotential is 135 mV@10 mA cm^{-2} and the tafel slope is 129.7 mV/dec). Accordingly, it can be inferred that the ECSA is correlated to HER performance of Co-W.

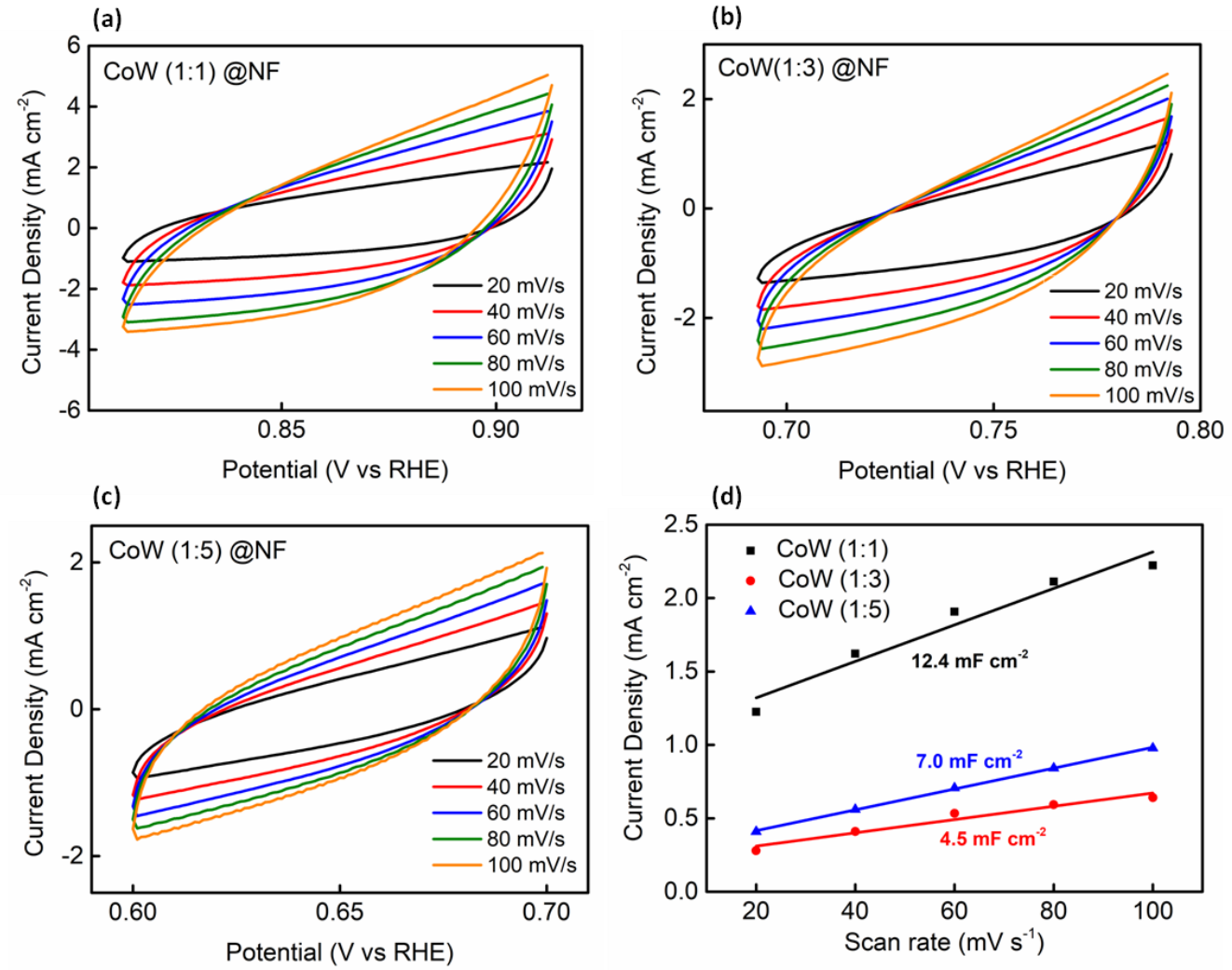

Fig. 12 a) CV of CoW (1:1) b) CV of CoW (1:3) c) CV of CoW (1:5) d) linear regression between the current density differences in the middle of the potential window of CV vs. scan rates for three CoW samples

3.5 Materials Characterizations

3.5.1 SEM Analysis

Morphology analysis was conducted on a scanning electron microscope (SEM). Fig. 13 shows that the morphology of Co-Mo (1:1) is round shape in the large scale. When the scale bar represents 300 nm, the sheet-shaped nanostructure is observed. In Fig. 14, Co-W (1:5) has the porous surface, which can significantly increase its surface area, leading to a better performance for both HER and OER.

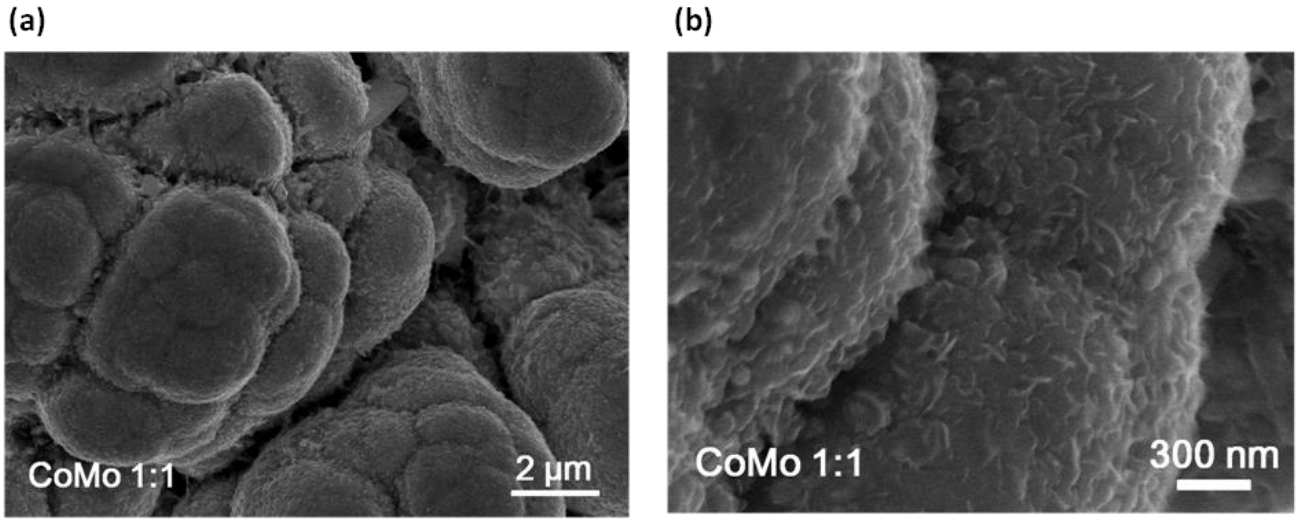

Fig. 13 SEM images of CoMo (1:1)

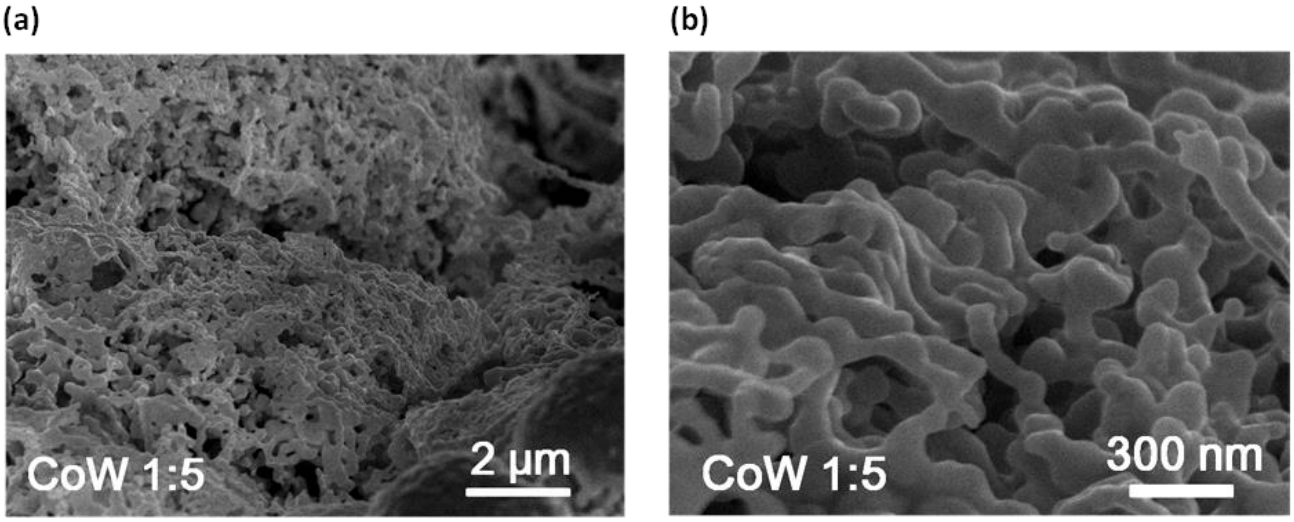

Fig. 14 SEM images of CoW (1:5)

2.5.2 XRD Analysis

X-ray diffraction is a non-destructive technique for analyzing the structure of materials, primarily at the atomic or molecular level. The XRD spectrums of Co-Mo and Co-W are shown below (Fig. 15 and Fig.16).

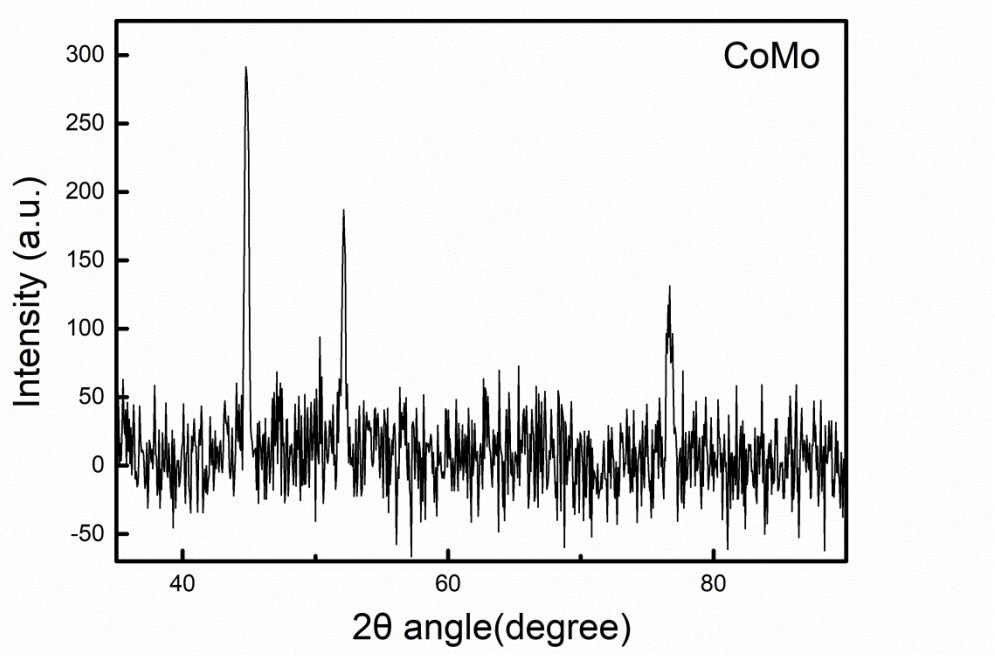

Fig. 15 the XRD spectrum of CoMo

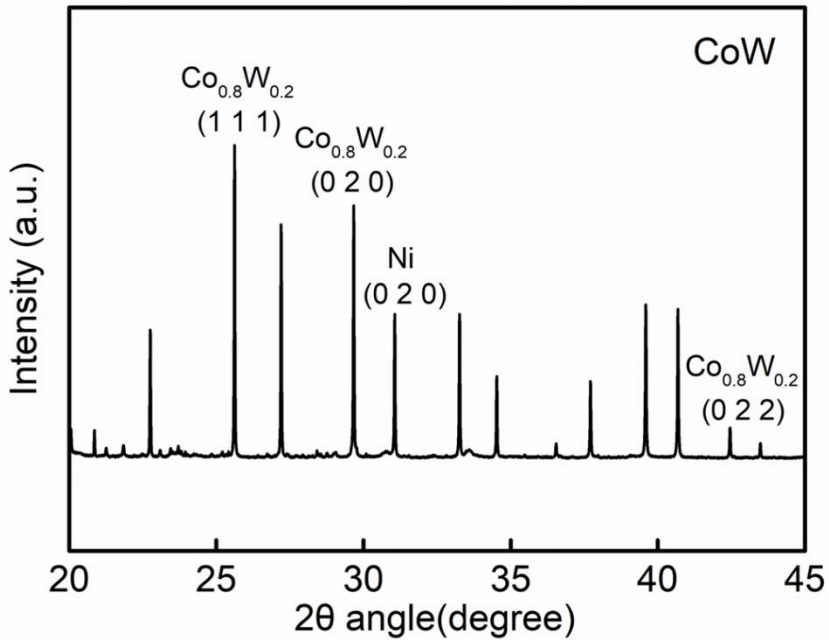

Fig. 16 the XRD spectrum of CoW

3.6 Comparison

In order to find the best electrocatalysts, Co, Co-Mo and Co-W are put on the same plot. Fig. 17 shows the LSV and tafel slope for HER. Fig. 18 shows the LSV and tafel slope for OER. In table 2 and 3, it shows that Co-Mo has the highest efficiency for both HER and OER, and then goes to Co-W. The last one is Co, which can prove the existence of synergistic effect.

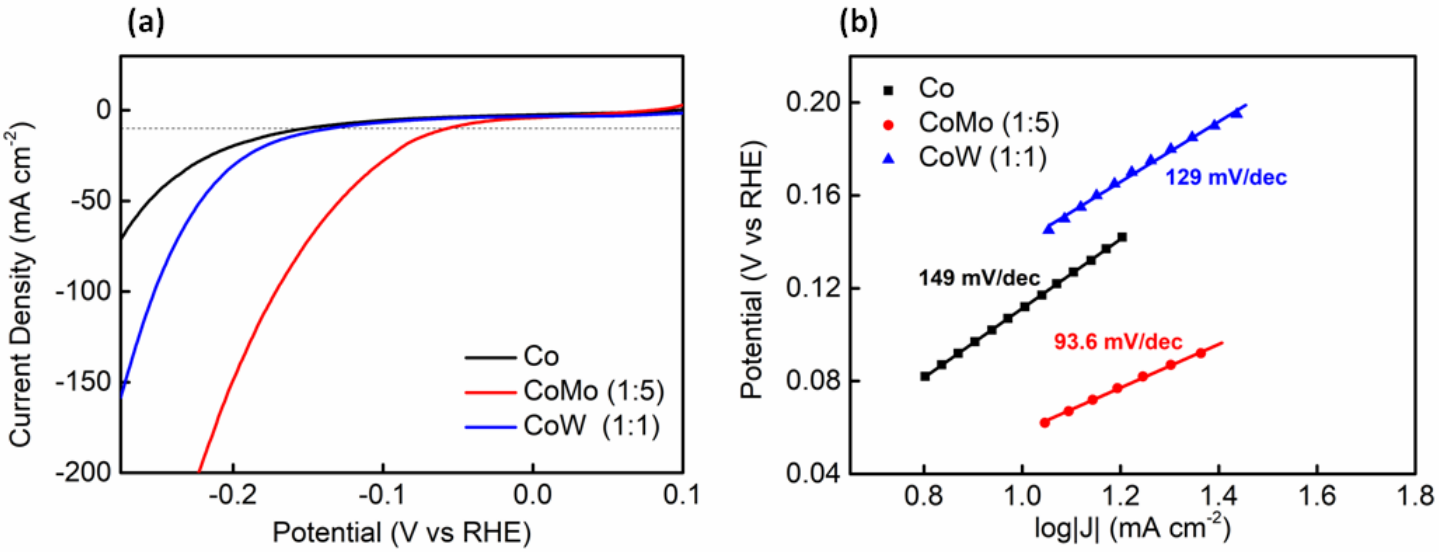

Fig. 17 a) LSV - Comparison of Co, CoMo and CoW b) Tafel - Comparison of Co, CoMo and CoW

Electrocatalyst	Overpotential (mV)	Tafel Slope (mV/dec)
Co	150	149
CoMo	56.8	93.6
CoW	135	129.7

Table 2 overpotential and tafel slope of Co, CoMo, and CoW for HER

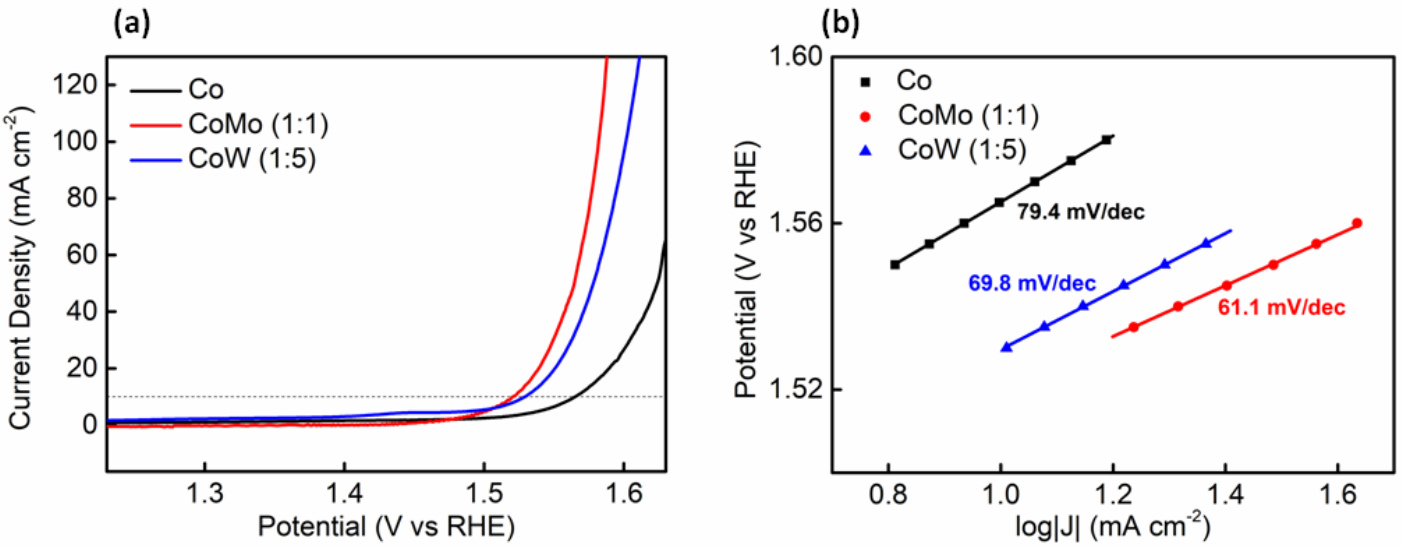

Fig. 18 a) LSV - Comparison of Co, CoMo and CoW b) Tafel - Comparison of Co, CoMo and CoW

Electrocatalyst	Overpotential (mV)	Tafel Slope (mV/dec)
Co	330	79.4
CoMo	290	61.1
CoW	299	69.8

Table 3 overpotential and tafel slope of Co, CoMo, and CoW for OER

4. Conclusion and Prospective

In this study, Co, Co-Mo and Co-W electrocatalysts have been successfully synthesized by electrodeposition after numerous attempts. Moreover, the composite catalysts show excellent bifunctional activities for HER and OER reactions. The characteristics of Co, Co-Mo, and Co-W electrocatalysts have been investigated thoroughly. Among these three catalysts, Co-Mo shows the best efficiency and activity for both HER and OER, and the least efficient electrocatalyst is Co. That is, the synergistic effect occurred in this experiment. Bimetallic electrocatalysts have advantages over monocatalysts due to it can catalyze H_2 and O_2 with less overpotential. Especially for OER, electrochemical properties of Co-Mo outperform some of the best electrocatalysts previously reported and make it promising candidate for overall electrochemical water splitting. Remarkably, these electrocatalysts are made by non-noble metals, which have the great potential to be produced on a commercial scale. Furthermore, this clean and renewable energy provides possible solution to the excess emission of greenhouse gasses.

5. Renferences

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利用 Co、Co/Mo、Co/W 等催化劑，催化水的分裂是非常有趣的題目。但也因為研究非常多，所以比較其他的成果也非常重要，尤其是催化效果、催化速率更需要比較。不是單單比較過電壓和阻抗大小而已。當然造價也是比較的條件之一。