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Electrochemical Synthesis of Electrocatalysts Ni-Fe, Ni-Co, Co-Fe double and Ni-Co-Fe Triple Hydroxides for Efficient Water Splitting to Oxygen and Hydrogen

by

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Abstract

In this study we have electrochemically fabricated the naturally abundant and stable electrocatalysts Ni-Fe, Ni-Co, Co-Fe-double hydroxides and Ni-Fe-Co-triple hydroxides, for efficient splitting of water to oxygen and hydrogen. Oxygen-evolution reaction (OER) activity of these electrocatalysts electrodeposited on different substrates were examined in an alkaline solution of potassium (KOH). The substrates used were Ni-foam, electrodeposited Ni-Co-oxide on Ni-foam and pressed porous Ni-Co oxide under varying electrodeposition bath composition, electrodeposition time under potential and current controls. The results clearly showed the pronounced effect of substrate on the electro-catalytic activity of these double and triple hydroxides. The synergetic effect of multiple hydroxides and the substrate is responsible for such enhanced electrocatalytic activity. We found that Ni-Fe-Co-triple hydroxide electrodeposited for total of 10 min under potential control at $-1.0/\text{SCE}$ on pressed porous Ni-Co-oxide sheet acted as an exceptional electrocatalyst for OER during water splitting reaction. This electrocatalyst generated a current density of $\sim 100.0 \text{ mA cm}^{-2}$ at an oxygen overpotential of 0.270 volt ($= 1.5 \text{ V vs RHE}$) in 1.0 M KOH at electrolyte temperature of 25°C . However, the triple hydroxide deposited for 7 min generated 81.0 mA cm^{-2} at the same overpotential and electrolyte temperature. However, among the double and triple hydroxides deposited on pressed porous Ni-Co oxide substrate under current control at -250 mA/cm^2 for 100 sec, the Co-Fe double hydroxide showed better performance generating a current density of $\sim 27.0 \text{ mA/cm}^2$ at an oxygen overpotential of 0.270 volt ($= 1.5 \text{ V vs RHE}$) in 1.0 M KOH electrolyte at room temperature. Thus, indicating that the activity of double or triple hydroxides synthesized under potential control electrodeposition were found higher compared to samples synthesized by current control perhaps due to too thinner film formation in 100 sec deposition time in the later.

Key Words: Water electrolysis, Hydrogen fuel, Electrocatalyst, Ni-Fe-hydroxide, Ni-Co-oxide, triple hydroxides, double hydroxides, Oxygen-evolution activity

Introduction

Climate change, global warming, and greenhouse gases have become a source of consternation for cities and nations around the globe. It is incumbent upon our humanity to save the planet earth from devastating global warming and climate change and at the same time maintain and advance our standard of living. Water electrolysis, using a sunlight-driven photoelectrochemical cell (PEC) and solar cell driven water splitting in an electrochemical cell (**Figure 1**) using electrocatalytic electrodes¹⁻² are the promising options for hydrogen production from renewable resources. Hydrogen is CO_2 emissions-free alternative fuel. Activity of electrocatalysts for water oxidation is fundamental for energy conversion technologies including integrated solar water-splitting devices.³⁻⁵ This will then be an effective way to store sun's near infinite energy in the form of hydrogen fuel.⁶⁻⁸

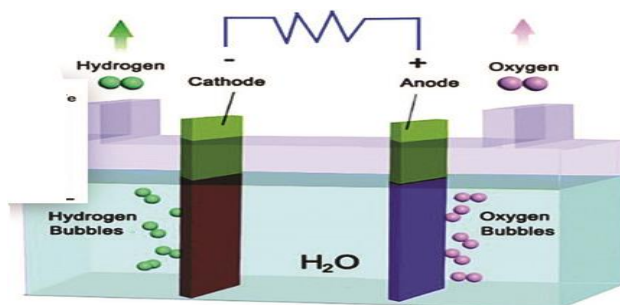
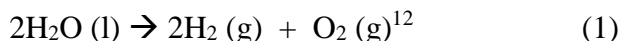


Figure 1: Schematic diagram of an electrochemical cell ⁹ showing water splitting to oxygen and hydrogen.

The abundant and cost-effective solar energy captured using optimum design of silicon-based solar cell modules¹⁰ can be used to generate the power required to drive the water electrolysis reaction. However, currently water electrolyser's have low current efficiency when compared to non-renewable CO₂ emitting sources, such as natural gas or methanol.¹¹ In an effort to improve water electrolysis efficiency, most researches have been focusing on the energetically challenging water oxidation to separate oxygen from water at anodes by oxygen evolution reaction (OER) and thereby facilitate hydrogen evolution reaction (HER) at cathodes during water splitting reaction as,



Recently, the use of Ni-hydroxide as an efficient anode received much attention for OER in alkaline medium¹³⁻¹⁶ and enhancement of electrocatalytic activity for OER when Fe was incorporated.¹⁴⁻¹⁷ The cathodically electrodeposited Ni-Fe hydroxides were extensively used for the OER in alkaline medium where the effect of electrolyte concentration and its temperature were explored.¹⁸ The mixed Ni-Co-oxide and mixed Ni-Co-Fe-oxides were also used or the efficient water splitting reaction.¹⁹

In this study, we have electrochemically fabricated naturally abundant and stable electrocatalysts, Ni-Fe, Ni-Co, Co-Fe-double and Ni-Co-Fe triple hydroxides for efficient splitting of water to oxygen and clean fuel hydrogen. Oxygen-evolution activity of these electrocatalysts deposited on various substrates such as Ni-foam, Ni-Co oxide electrodeposited on Ni-foam, and pressed porous Ni-Co-oxide, were examined in an alkaline solution of 1.0 M KOH. We hypothesized that the synergetic effect of mixed hydroxide can have pronounced electrocatalytic activity for the oxygen evolution reaction during water splitting reaction to oxygen and hydrogen.

Experimental

1. Synthesis of pressed porous Ni-Co-oxide substrate

The mixture of Ni metal powder and cobalt oxide powder in presence of aluminum powder and zinc dust were pressed under suitable pressure and sintered at 800 °C in an electric furnace for 4 hours under an inert argon gas atmosphere. The sample was then acid leached to make it porous by removing the zinc dust and aluminum powders.

2. Synthesis of substrate Ni-Co-oxide on Ni-Foam

Ni-Co-double hydroxide using bath composition of 2 mM Ni (NO₃)₂ and 4 mM Co (NO₃)₃ was deposited on HCl acid clean Ni-foam by applying -1.0 volt/SCE for 600 sec using Ni-Foam as the counter electrode. This hydroxide was then oxidized to form oxide in an electric oven at 300 °C for 2 hours.

3. Electrodeposition of Ni-Fe-double and triple hydroxides on Ni-Co-oxide on Ni-foam under voltage control

Electrodeposition of Ni-Fe-hydroxide was carried out under cathodic voltage of -1.0 V/SCE for electrodeposition time of 420 sec (7 min) on different substrates except one deposited for 10 min.

Electrodeposition bath composition: For double hydroxide: 2 mM Fe (NO₃)₃ (anhydrous) + 2 mM Ni (NO₃)₂. For triple hydroxide: 2 mM Fe (NO₃)₃ (anhydrous) + 2 mM Ni (NO₃)₂ + 2.6 mM Co (NO₃)₂

4. Electrodeposition of Ni-Fe-double and triple hydroxides on pressed porous Ni-Co-oxide and on bare Ni-Foam

I. Voltage Control Electrodeposition

Electrodeposition of Ni-Fe-double and Ni-Fe-Co-triple hydroxides were carried out under voltage control cathodic voltage of -1.0 V/SCE for the electrodeposition time of 420 sec (7 min) on different substrates.

Electrodeposition bath composition: For Ni-Fe-double hydroxide: 9 mM FeSO₄ (anhydrous) + 9 mM NiSO₄. 6H₂O + 25 mM (NH₄)₂SO₄. For Ni-Co double hydroxide: 9 mM NiSO₄. + 9 mM CoSO₄ 6H₂O + 25 mM (NH₄)₂SO₄. For Co-Fe double hydroxide, 9 mM CoSO₄ + 9 mM FeSO₄ + 25 mM (NH₄)₂SO₄, and For Triple hydroxide: 9 mM FeSO₄ (anhydrous) + 9 mM NiSO₄. 6H₂O + 9 mM CoSO₄ +(25 mM (NH₄)₂SO₄.

II. Current Control Electrodeposition

Electrodeposition of Ni-Fe-hydroxide and Ni-Co-Fe-triple hydroxides was carried out under cathodic current of -250 mA cm^{-2} with Ni-foam as counter electrode for 100 sec.

Electrodeposition bath composition: For double hydroxide: 9 mM FeSO_4 (anhydrous) + 9 mM $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ + 25 mM $(\text{NH}_4)_2\text{SO}_4$. For Triple hydroxide: 9 mM FeSO_4 (anhydrous) + 9 mM $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ + 9 mM CoSO_4 + (25 mM $(\text{NH}_4)_2\text{SO}_4$

5. Determination of oxygen evolution reaction (OER) rate during Water Splitting

The OER rates in terms of current density, in electrolyte solution of 1.0 M KOH at electrolyte temperature of 25 °C, and at room temperature were measured using EG&G Princeton applied research potentiostat/galvanostat controlled by Versastat-3 software in an electrochemical cell as shown in Figure 1. The results are of OER rate on different electrocatalyst electrodes as current density versus potential versus saturated calomel electrode (SCE) were measured using linear voltammetry at a scan rate of 5 mV/sec.

Results and Discussion

Figure 2 shows The oxygen evolution current versus oxygen overpotential on Ni-Fe -double and Ni-Co-Fe-triple hydroxides synthesized by electrodeposition under voltage control at cathodic voltage of -1.0 V/SCE for 10 min at room temperature on various substrates such as Ni-foam, Ni-Co-oxide on Ni-foam and on pressed porous Ni-Co-oxide in 1 M KOH at electrolyte temperature of 25 °C measured using a scan rates of 5 mV/sec. The results show that Ni-Co-Fe triple hydroxide deposited on pressed porous Ni-Co oxide acts as a superior electrocatalyst for OER exhibiting a current density of 100 mA/cm^2 at oxygen overpotential of 0.270 mV which is 1.5 V vs RHE. Also, Ni-Fe double hydroxide deposited on pressed porous Ni-Co oxide shows better performance for OER exhibiting a current density of 39 mA/cm^2 at oxygen overpotential of 0.270 mV which is 1.5 V vs RHE compared to it deposited on clean Ni-foam which gives only 6.0 mA/cm^2 at the same overpotential.

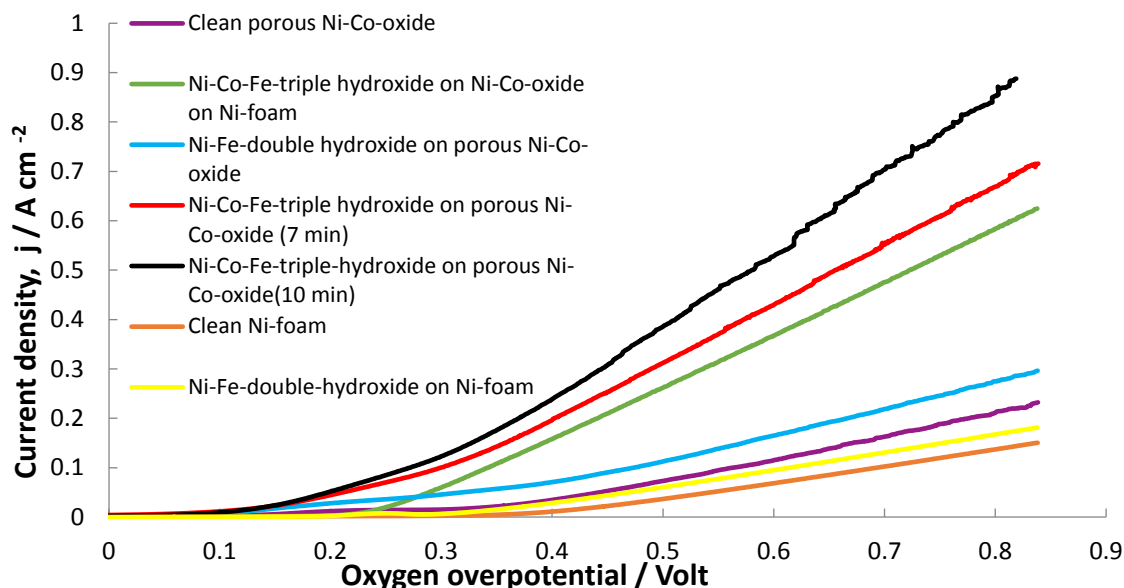


Figure 2: The oxygen evolution reaction (OER) current density versus oxygen overpotential on Ni-Fe -double and Ni-Co-Fe-triple hydroxides synthesized by electrodeposition under voltage control at cathodic voltage of -1.0 V/SCE for 10 min at room temperature on various substrates such as Ni-foam, Ni-Co-oxide on Ni-foam and on pressed porous Ni-Co-oxide in 1 M KOH at electrolyte temperature of 25 °C measured using a scan rates of 5 mV/sec.

Figure 3 shows the current density for OER versus oxygen overpotential at Ni-Fe, Ni-Co, Co-Fe - double and Ni-Co-Fe - triple hydroxide electrocatalyst electrodes electrodeposited on porous Ni-Co-oxide under cathodic current control at -250 mA/cm^2 for 100 sec measured in 1 M KOH at room temperature at a scan rate of 5 mV/sec. Among these double and the triple hydroxides, the Co-Fe double hydroxide shows better electrocatalytic activity toward OER during water splitting exhibiting a current density of 27 mA/cm^2 at oxygen overpotential of 0.27 V ($= 1.5 \text{ V/RHE}$) in 1 M KOH.

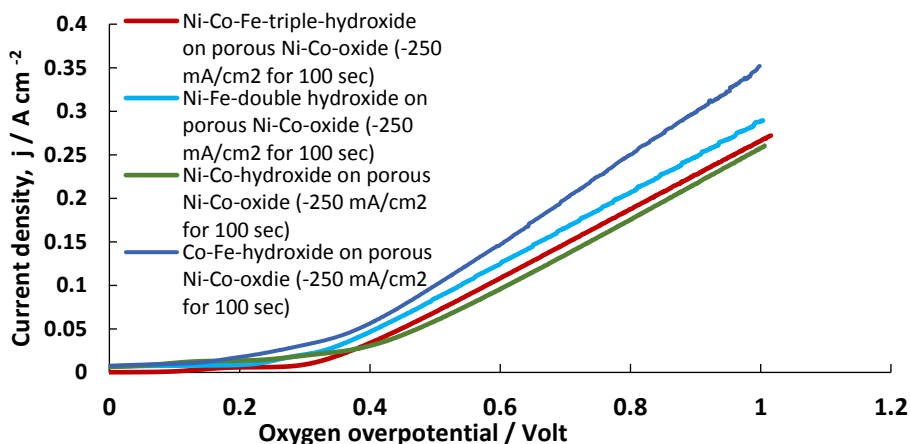


Figure 3: The current density for OER versus oxygen overpotential at Ni-Fe, Ni-Co, Co-Fe - double and Ni-Co-Fe - triple hydroxide electrocatalyst electrodes electrodeposited on porous Ni-Co-oxide under cathodic current control at -250 mA/cm^2 for 100 sec measured in 1 M KOH at room temperature at a scan rate of 5 mV/sec.

Conclusion

This study reveals that the synergetic effect and the morphology of the substrate on which the Ni-Fe-double hydroxide or Ni-Fe-Co-triple hydroxide were electrodeposited played a vital role in enhancing the OER rate during water splitting reaction. The effect of higher electrolyte temperature was found important in enhancing the OER rate during water splitting. The Ni-Fe-Co triple hydroxide electrodeposited on pressed porous Ni-Co-oxide substrate for total of 10 min under potential control of -1.0 volt/SCE acted as a superior electrocatalyst for oxygen evolution during water splitting reaction. (**Figure 2**). This electrocatalyst generated a current density of 100.0 mA cm^{-2} at an oxygen overpotential of 0.270 volt (= 1.5-volt vs RHE) in 1.0 M KOH at electrolyte temperature of 25 °C.

However, the Ni-Fe-double hydroxide electrodeposited on pressed porous Ni-Co-oxide substrate for total of 10 min under potential control of -1.0 volt/SCE generated a current density of 39.0 mA cm^{-2} at an oxygen overpotential of 0.270 volt (= 1.5-volt vs RHE) in 1.0 M KOH at electrolyte temperature of 25 °C. Future studies should focus on optimizing the current density for current control or voltage for voltage control electrodeposition, the electrodeposition time and the deposition bath composition and concentration to have pronounced activity of electrocatalysts for enhanced rate of OER during water splitting to oxygen and hydrogen. Future studies should be focused on determining the activity and stability of the electrocatalysts at 25 °C and at elevated temperature (e.g., 50 °C) and at higher electrolyte concentrations (e.g., 6.0 M) to design and fabricate a viable water electrolyzer for efficient water splitting to hydrogen fuel powered by solar panel and/or by solar wind power. Integrating solar energy and wind power as sources to bias the electrolyzer for water splitting reaction will make hydrogen production from water carbon footprint free.

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