Research Article

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Electrocatalytic Properties of Ni-Doped $\text{BaFe}_{12}\text{O}_{19}$ for Oxygen Evolution in Alkaline Solution

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Abstract: Transition metal oxide (TMO) continues to be studied and developed as an oxygen evolution reaction (OER) electrocatalyst due to its abundance and low price. The aim of this experiment was to evaluate Ni²⁺-doped $\text{BaFe}_{12}\text{O}_{19}$ (BHF) as an OER electrocatalyst in an alkaline medium. BHF and Ni-doped BHF was synthesized through a low temperature coprecipitation technique followed by a calcination process at 750°C for 4 h. Diffractograms of the BHF and the Ni-doped BHF indicated a single phase on the synthesized BHF and formed Fe_2O_3 impurities on the Ni-doped BHF. SEM images showed a homogenous plate-shaped particles in the BHF, while the Ni-doped BHF had larger inhomogeneous particles. Ni dopant increased OER electrocatalytic activity of BHF based on overpotential on specific current density. The Ni-doped BHF had comparable activity to some metallic oxides based on their overpotential values at specific current density value.

Keywords: BHF; Ni-doped BHF; co-precipitation; OER electrocatalyst.

1 Introduction

Oxygen evolution reactions (OER) and oxygen reduction reactions (ORR) are the basic anodic reaction processes

and are essential for applications in energy storage and conversion. Oxygen evolution mechanisms require a large overpotential to drive the reaction at practical rates, so that some extra energy is dissipated. Noble metals and their oxides (Pt, Ru, and Ir) are known as the best and most stable electrocatalysts for oxygen evolution. The limited sources and high cost of these noble catalysts have been the major obstacle to adoption for mass markets. Therefore, it is highly desirable to develop sustainable and low-cost OER and ORR catalysts for applications in energy storage and conversion.

Transition metal oxides (TMO) with spinel-structure [1-4] and perovskite-structure [5-7] have been widely investigated recently and characterized for OER and ORR. NiFe_2O_4 phase in mixed oxide Ni-Fe has been shown to have a significant role in improving the oxygen evolution activity in 1M NaOH solution [1]. $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ was found to be an active electrocatalyst for oxygen evolution reaction in 1 M KOH with Tafel slope values of 44 mVdecade⁻¹. Other ferrite types such as barium hex ferrites ($\text{BaFe}_{12}\text{O}_{19}$) are commonly used as magnetic materials and have excellent chemical stability and corrosion resistivity. Zn²⁺-doped $\text{BaFe}_{12}\text{O}_{19}$ nanoplate (2.7 mole% Zn²⁺, thickness ca. 50 nm) demonstrated a reversible capacity of 665.5 mA h g⁻¹ after 250 cycles at current density of 100 mA g⁻¹ as anode materials for lithium-ion batteries (LIBs) [8]. Zn²⁺-doping is beneficial to increase the electronic conductivity of $\text{BaFe}_{12}\text{O}_{19}$, and improving the cycling performance. Other Ni-Fe-based electrocatalysts have been under intense study, especially Ni-Fe oxy-hydroxide forms, because they are the most active catalysts measured in basic media [9-11]. OER activity of first-row transition metal oxyhydroxide thin films are $\text{Ni}(\text{Fe})\text{O}_x\text{H}_y > \text{Co}(\text{Fe})\text{O}_x\text{H}_y > \text{FeO}_x\text{H}_y > \text{AuO}_x > \text{FeO}_x\text{H}_y > \text{CoO}_x\text{H}_y > \text{NiO}_x\text{H}_y > \text{MnO}_x\text{H}_y$. The phase of $\text{Ni}_{0.9}\text{Fe}_{0.1}\text{OOH}$ has an OER turnover frequency (TOF) more than 10-fold higher than that of IrOx. Incorporation of Fe impurities in $\text{Ni}(\text{OH})_2/\text{NiOOH}$ is responsible to increased activity of aged $\text{Ni}(\text{OH})_2/\text{NiOOH}$ [10]. In addition, precipitation of Fe in $\text{Ni}(\text{OH})_2/\text{NiOOH}$ will form $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_2/\text{Ni}_{1-x}\text{Fe}_x\text{OOH}$ phase which has a higher conductivity than $\text{Ni}(\text{OH})_2/\text{NiOOH}$, up to 30-fold [10].

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In this work, we studied Ni^{2+} -doped $\text{BaFe}_{12}\text{O}_{19}$ that was synthesized through a low temperature coprecipitation technique followed by a calcination process, as a catalyst for OER in an alkaline medium. The motivation of this work is to increase electronic conductivity of $\text{BaFe}_{12}\text{O}_{19}$ and form complex Ni-Fe oxyhydroxides on the catalyst surface, to improve the catalytic performance.

2 Experimental

2.1 Materials

Barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were all purchased from Merck Ltd. All chemicals were of analytical grade and were used as received without further purification.

2.2 Electrocatalyst Preparation

The $\text{BaFe}_{12}\text{O}_{19}$ was synthesized by a low temperature coprecipitation technique that is modification of previous method [12]. The mixed solution of 2.1977 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (9 mmol) and 29.1866 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (108 mmol) in 40 mL of 0.6 M HCl was slowly introduced dropwise into 150 mL of 1.5 M NaOH solution. During the addition of the mixed solution, the temperature of reaction was constantly maintained within 3–4 °C with a circulating thermostatic bath and the solution was vigorously stirred. The dark brown precipitate immediately appeared as the mixed solution was added. The precipitate was centrifuged at 3500 rpm for 15 min. The precipitate was dried at 150 °C for 4 h, calcined at 750 °C for 4 h and washed with deionized water until free of chloride ion to obtain crystalline $\text{BaFe}_{12}\text{O}_{19}$. The preparation procedure of Ni^{2+} -doped $\text{BaFe}_{12}\text{O}_{19}$ was the same as that of $\text{BaFe}_{12}\text{O}_{19}$ with precursor compositions of 1:11.6:0.4 (BHFNi0.4) for $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}:\text{FeCl}_3 \cdot 6\text{H}_2\text{O}:\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1:8:4 (BHFNi4) for $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}:\text{FeCl}_3 \cdot 6\text{H}_2\text{O}:\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively.

2.3 Characterizations of Electrocatalysts

The barium hexaferrite structure was determined by XRD GBC EMMA software Traces 28 mA, 35 kV with $\text{Cu K}\alpha$ 1.54056 Å in the 2θ of 10–90°, step size of 0.02°, and scan rate of 2°/min. Functional groups of products

was determined by using a Prestige-21 Shimadzu FTIR spectrometer. The morphologies of the samples were examined by using a JOEL scanning electron microscope (SEM) JS-IT100. The thermal properties of the precipitate were measured using DTA/TG under air purge with a temperature raising rate of 5 °C/min.

2.4 Electrocatalytic Activity

The catalyst slurries were prepared using polyvinyl acetate (PVAC) as a binder, and isopropanol as the solvent. The slurries were prepared by mixing of 50 mg material catalyst and 10 μL of 5% PVAC solutions in water-isopropanol (1:1), stirred to homogenous, and then dripped on the surface of SPCE DS-110. All the electrochemical analyses, such as cyclic voltammograms (CV) and Tafel polarization, were performed in a conventional three-electrode single compartment Pyrex glass cell using a computerized potentiostat (DY 2300 Digi-ivy). Polarization potential was measured in 1M NaOH solution with Ag/AgCl electrode as a reference electrode, platinum wire as an auxiliary electrode, and BHF electrocatalyst as a working electrode. Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

3.1 Characteristics of $\text{BaFe}_{12}\text{O}_{19}$ and Ni-doped $\text{BaFe}_{12}\text{O}_{19}$

XRD patterns of BHF synthesized by co-precipitation method at low temperatures with and without washing before calcination process are presented in Figure 1. The results showed that single phase of $\text{BaFe}_{12}\text{O}_{19}$ was obtained from the precipitates calcined at 750 °C for 4 h and then washed with deionized water until free from chloride ion. This result is in line with previous research using the co-precipitation technique at 0 ± 1 °C using FeCl_3 and BaCl_2 as precursors [12]. In this method, formation of BHF at this condition was assisted by the presence of NaCl in the precipitate which served as a flux in the formation of $\text{BaFe}_{12}\text{O}_{19}$ crystals. The function of NaCl as a flux is evidenced by the absence of BHF in product calcinated at 750 °C for 4 h that was prepared through washing of precipitate before calcination (Figure 1 c). It took a longer time at the calcination temperature of 750 °C or needed higher temperature to form BHF crystals. Other evidence that NaCl served as the flux can also be seen in Figure

Figure 1: Diffraction patterns of the washing effect before calcination on the formation of BHF.

1 b which exhibits presence of BHF peak in the product that prepared from precipitate without washing that was calcinated at 750°C for 2 h. The effect of NaCl flux to accelerate crystal formation BHF has been previously studied [13,14]. The salt is used since the metal oxide is more soluble in molten metal chloride of groups IA and IIA, compared to other forms. The metal oxides in the flux undergo rearrangement and diffuse to form the expected phase [13,14].

X-Ray diffraction pattern of $\text{BaFe}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x=0$, $x=0.4$, $x=4$) shows M-type hexaferrite crystal and a single-phase

hexagonal structure as depicted in Figure 2. Meanwhile, the visualization of the BHF structure from Rietveld process is shown in Figure 3 using VESTA software. Distance and angle of inter atom O-Fe in BHF is difference depend on its atomic geometry and position. The unit cell parameters and cell volume of all samples are listed in Table 1. It was found that the lattice constant and cell volume decrease with the presence of Ni dopant. It is related to the replacement of the higher ionic radius of Fe^{3+} (0.078 nm, octahedral, high spin) by the lower ionic radius of Ni^{3+} (0.074 nm, octahedral, high spin). Substitution of

Figure 2: XRD pattern of BHF (Top), $\text{BaNi}_{0.4}\text{Fe}_{11.6}\text{O}_{19}$ (middle) and $\text{BaNi}_4\text{Fe}_8\text{O}_{19}$ (bottom).

Table 1: Lattice parameters of the synthesized materials.

Phase	Cell unit			Crystallite size (nm)	
	a=b (Å)	c(Å)	V (Å ³)	WH	Langford
$\text{BaFe}_{12}\text{O}_{19}$	5.89381	23.20737	698.1494	116.9(4.9)	143.6 (2.9)
$\text{BaNi}_{0.4}\text{Fe}_{11.6}\text{O}_{19}$	5.89454	23.19318	697.8961	33.1(0.7)	36.0(0.6)
$\text{BaNi}_4\text{Fe}_8\text{O}_{19}$	5.89338	23.19432	697.6548	46.6(0.6)	50.9(0.5)

Ni element caused contraction of the crystal structure of the barium hexaferrite, resulted in a decreasing size of the crystallite. It is indicated by the presence of peak broadening and intensities decreasing in the XRD pattern of the Ni-doped $\text{BaFe}_{12}\text{O}_{19}$.

Infrared spectra for the precipitates and the powder calcinated at 750°C are shown in Figure 4. The dried precipitate spectrum illustrates the presence of absorption bands at 3331 cm^{-1} attributed to the O-H stretching of water and of the metal hydroxide. The distinctive OH-bending

Figure 3: Visualization of refined barium hexaferrite using Vesta software.

doublet associated with goethite (α -FeOOH) at 771 and 941 cm^{-1} were observed along with well-defined peaks corresponding to Fe-O lattice vibrations at lower frequencies (607 and 476-463 cm^{-1}) [15]. The absorption bands at 590 cm^{-1} , 543 cm^{-1} , and 437 cm^{-1} belong to the metal-oxygen stretching vibrations of the $\text{BaFe}_{12}\text{O}_{19}$ and of the Ni-doped $\text{BaFe}_{12}\text{O}_{19}$.

BHF formation from the precipitate precursor was studied through DTA/TGA thermal characterization. Intermediate phases of BHF synthesis using co-precipitation method are not clearly known. $\text{Ba}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, NaCl and its hydrated hydroxide are precipitates that resulted from coprecipitation process using BaCl_2 and FeCl_3 as the precursors and the NaOH as the precipitating agent. Thermal properties of the BHF dried precipitates showed endothermic peaks at 76.4°C, 638°C, and 805°C, and an exothermic peak at 735°C (Figure 5a). At temperature ranges of 200-800°C, the weight loss of approximately 10% indicates the phase transition from the precipitates to barium hexaferrite. This DTA/TGA plot is in line with the thermogram of the dried precipitates resulting from $\text{Ba}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ as the precursors

and a NaOH- Na_2CO_3 system as the precipitating agent [16]. Strong endothermic peak at 805°C can be attributed to the melting point of NaCl in the precipitates. The onset temperature, which reflects the melting point, matches well with the value of 801°C in the previous study [17]. The DTA/TGA curves of Ni-BHF have a similar pattern to the DTA/TGA curves of the BHF, i.e. there are endothermic peaks at 76.4°C, 638°C, and 805°C, and an exothermic peak at 735°C (Fig 5b,c).

The morphology of the BHF and Ni-doped BHF was examined by scanning electron microscope (SEM). Figure 6a shows that co-precipitation technique followed by calcination at 750°C resulted in some nanoplates of BHF ca. 70-140 nm in thickness and ca. 400-600 nm in diameter. The plate shape in this result agrees with the findings of others [12,18,19]. Homogeneous grain size is shown in the SEM image of the BHF, meanwhile the Ni-doped BHF tends to agglomerate, be inhomogeneous and larger in size than that of the BHF (Figure 6b). It indicates that the particle size distribution of the BHF was influenced by the Ni doping. Increasing grain size also occurs in Zn-Nb substituted BHF synthesized via sol-gel technique [18].

Figure 4: FTIR spectra of the dried precipitate (purple), $\text{BaFe}_{12}\text{O}_{19}$ (red), $\text{BaNi}_{0.4}\text{Fe}_{11.6}\text{O}_{19}$ (blue) and $\text{BaNi}_4\text{Fe}_8\text{O}_{19}$ (black).

Figure 5: DTA/TG curves of the dried precursors for (a) BHF, (b) BHFNi_{0.4}, (c) BHFNi₄.

Figure 6: SEM image of BHF (a) and Ni-doped BHF (b) synthesized by coprecipitation technique.

3.2 Electrochemical Study

The electrocatalyst stability of the BHF and the N- doped BHF were measured in the potential range of -1 - 1 (V vs Ag / AgCl) with a scan rate of 0.05 V/sec and sensitivity of 0.001 A/V in 1M NaOH medium. The electrocatalysts appeared to be stable during electrochemical measurements using the cyclic voltammetry of 20-cycles, so that the measurement could be continued to determine the catalytic activity of the OER (supplementary 1). SPCE DS-110 and PVAC binder were used to improve sensitivity and stability of electrocatalytic measurements from catalysts. PAVC has been studied as a binder in electrochemical applications, such as binders in the fabrication of LiFePO₄ composite cathodes for lithium batteries [20] and binders in WO₃/BiVO₄ photoanodes for solar water splitting [21]. PVAC is categorized as an eco-friendly binder and could replace fluorinated polymers such as PVDF and Nafion. In Figure 7c, cyclic voltammograms of BHF and Ni-doped BHF showed microelectrode pattern, which oxidation and

Figure 7: Electrochemical parameters of BHF and Ni-doped BHF in 1M NaOH.

reduction peaks were not observed. This is in line with cyclic voltammograms of La_{0.9}Ca_{0.1}Co_{1-x}Fe_xO₃ cathode [22] and Cu_xCo_{3-x}O₄ for oxygen evolution reaction [23]. Electrochemical measurement showed changes in Tafel slope (b), exchange current density (J_0), overpotential (h), and charge transfer coefficient (a) after the SPCE was modified using the BHF and the Ni-doped BHF. The Tafel slope (b) for the BHF was still large up to > 500 mV/dec and decreased, reaching 179 mV/dec with the presence of Ni dopant (Figure 7 and Table 2). On the other hand, Ni dopant also decreased the BHF overpotential at 10 mA/cm² from 393 mV to 180 mV in 1 M NaOH medium. The BHF doped with Ni_{0.4} and Ni₄ had comparable activity to some metallic oxides based on their overpotential values at specific current density values. Overpotentials of IrO₂ and RuO₂ at 10 mA/cm² current densities in 0.5 M KOH are 358 mV and 411 mV, respectively. Several spinel ferrites have been studied for the catalytic activity [24] and the tendencies are CoFe₂O₄ > CuFe₂O₄ > NiFe₂O₄ > MnFe₂O₄.

In addition, NiFe oxides in layer form such as oxyhydroxide have a high OER activity. Fe-doped nanocrystallized nickel oxide (Fe_xNi_{1-x}O) was synthesized as an OER electrocatalyst in an alkaline medium [25]. The Fe_{0.1}Ni_{0.9}O has the highest electrocatalytic value for water oxidation with turn-over frequency (TOF) of 1.9 s⁻¹ at 300 mV overpotential. The 10 mA/cm² current density is achieved at 297 mV overpotential and has a Tafel slope of 37 mV dec⁻¹. The performance of the iron oxide nickel and the evidence of this study indicates that the electrocatalytic performance of the Ni-doped BHF is due to the presence of redox complex systems of Fe²⁺/Fe³⁺, Fe³⁺/Fe⁴⁺ and Ni²⁺/Ni³⁺.

The OER electrocatalytic capability of the BHF may be due to the non-stoichiometric (defect) of Fe atoms, the occurrence of oxygen vacancy, and the geometry of Fe atoms. The defect of Fe atoms may cause destabilization of the crystal structures, resulting in M-O-M angular changes. The presence of oxygen vacancy can facilitate the formation of OH absorption in Fe atoms. The different geometry of Fe (octahedral, tetragonal and trigonal bipyramidal) affects the composition and position of electrons in different d (e_g and t_{2g}) orbitals, as well as the strength and length of the M-O bonds. Based on VESTA visualization, bond of Fe-O in octahedral and trigonal bipyramidal are longer than tetrahedral geometry (Figure 3). Fe-O bond has different length on octahedral at D position, tetrahedral, and trigonal pyramidal, so these are predicted as active site of electrocatalyst.

The Fe³⁺ orbital profiles in octahedral, tetrahedral, and trigonal bipyramidal geometries are presented in Figure 8. The oxidation state and the spin type of the

Table 2: Measurement and kinetic parameters for BHF, Ni-doped BHF, and other electrocatalysts for OER.

Material	Electrolyte	Substrate	Overpotential (mV) at $j_0=10$ mA/cm	Tafel slope (mV dec ⁻¹)	charge transfer coefficient (α)	Remarks
BHF	1 M NaOH	Carbon	393	503	0.117	This study
BHFNi _{0.4}	1 M NaOH	Carbon	174	180	0.328	This study
BHFNi ₄	1 M NaOH	Carbon	180	179	0.33	This study
RuO ₂	0.5 M KOH	FTO	358	55		[24]
IrO ₂	0.5 M KOH	FTO	411	91		[24]
NiFe ₂ O ₄	0.1 M KOH	GCE	440	-		[24]
NiFe ₂ O ₄	1 M KOH	Ni	-	42		[24]
CoCr ₂ O ₄	1 M KOH	GCE	422	63.3		[24]
CoCr ₂ O ₄ /CNT	1 M KOH	GCE	326	51		[24]

Figure 8: Splitting of Fe^{3+} orbital based on crystal field theory.

transition metal complex indicate the tendency of the chemical sorption force of the perovskite compound, and the octahedral geometry of the Fe^{3+} ion is more dominant in the BHF structure. This may cause the electrocatalytic activity of the BHF and the Ni-doped BHF. In addition, Fe ions undergo deformation to oxy-hydroxide (FeOOH) due to the adsorption of OH ions in the alkaline medium, which are in line with the following mechanisms of oxygen evolution [24,26]:

(i) Bockris Mechanism: **(ii) Bockris&Otagawa's:**

(iii) Krasil'shchikov's:

The Ni-doped BHF will result in a Fe³⁺/Fe⁴⁺ and Ni²⁺/Ni³⁺ redox system which is assumed to be an active site on the electrocatalyst, whereas on the BHF there is only one active site on the electrocatalyst. Introduction of Fe into Ni oxy-hydroxide increases the Ni²⁺/Ni³⁺ potential and decreases the potential onset for the catalyst [27]. Another review of the catalytic activity of Fe and Ni can be seen from the strength of the M-OH bond based on the enthalpy of its formation. The higher enthalpy of M-OH formation the lower the current density by the tendency of Ni > Co > Fe > Mn > Cr > V [28].

4 Conclusion

BHF and Ni-doped BHF have been successfully synthesized using coprecipitation techniques with BaCl₂ and FeCl₃ precursors without washing/neutralizing process before sintering at 750°C. NaCl in precipitate of BHF assisted in formation of BHF crystal and act as flux. The Ni-doped BHF and the BHF on SPCE surface had OER electrocatalytic activity in NaOH medium with good performance based on the overpotential value at specific current density.

Conflict of interest: Authors declare no conflict of interest.

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