



High efficiency water oxidation using NiAlFe-layered double hydroxides

Kamellia Nejati ¹, Leila Jafari Foruzin ^{2*}

¹ Department of Chemistry, Payame Noor University, P.O. Box 19395-3697, Tehran, Iran

² Inorganic Chemistry Laboratory, Department of Chemistry, Faculty of Sciences, Azarbaijan Shahid Madani University, Tabriz 53714-161, Iran.

E-mail: l.jafari @azaruniv.ac.ir , l.jafarie@gmail.com

Received: 2023-12-16, Accepted: 2024-05-03

Abstract

We report that ternary nickel-alumina-iron Layered Double Hydroxide (NiAlFe-LDH) is a highly active and stable oxygen evolution catalyst at neutral solutions. The LDHs were prepared using the co-precipitation method and were characterized by a field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD). According to powder X-ray diffraction and field emission scanning electron microscopy, NiAlFe-LDH exhibit a nanosized plate-like morphology with a basal space (d_{003}) of 7.64 °Å. Then amount of Al³⁺ at NiAlFe-LDH optimizes and the electrocatalytic activities of ternary-component were studied toward water oxidation in neutral solutions. The result compared with binary NiFe-LDH and NiAl-LDH. The obtained results show that the electrocatalytic activity of the ternary-component NiAlFe-LDH is much better than that of the binary-component NiFe-LDH and NiAl-LDH. The high electrocatalytic activity of ternary-component LDH may be attributed to the co-existence of Al and Fe active sites.

Keywords: Water Oxidation, Layered Double Hydroxide, Oxygen Evaluation, NiAlFe-LDH

Introduction

Increasing need to energy and environmental problems have motivated extensive study in several energy storage(Omer, 2009; Wang et al., 2022) .

In order to product energy by chemical fuels, water oxidation is the anodic half-reaction (in alkali: $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$) and neutral or acidic solution: $(2 \text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-)$) oxygen reduction reaction (ORR). The water oxidation is slow reaction (overpotential about 1.23 V need for this reaction) and various catalyst need to improve efficiency(Kubendhiran et al., 2023; Quang et al., 2022). For water electrolysis, the energy loss at the anode is significant because water oxidation requires four-electron transfer(Nai et al., 2015). Therefore, it is highly desirable to design efficient oxygen evolution reaction (OER) catalysts and ensure their assembly into practical OER electrodes. RuO_2 and IrO were active catalyst for water oxidation but scarcity and expensive cost's limited their use at water oxidation industry (Ping et al., 2016; Tang et al., 2014). So, study for achieve high yield with low cost in water oxidation is urgently required.

Layered double hydroxides (LDHs) are anionic clays, which are made of layers of

trivalent and divalent metal cations connected to the OH^- anions, with interlayer anions carbonate and nitrate inserted between the layers (Guo et al., 2010; Wang & O'Hare, 2012). LDH has been used in a variety of areas, including but not limited to catalysis, energy storage, drug or gene delivery, water treatment, etc (Alcantara et al., 2010; Fan et al., 2014).

Researches have showed that the octahedral MO_6 layers in 2D metal oxides/hydroxides are suitable catalysts for Oxygen generation (Nayak et al., 2015). One of 2D metal hydroxides is the layered double hydroxides (LDHs). Their chemical formula is $[\text{M}^{2+(1-x)} \text{M}^{3+x} (\text{OH})_2]^{\text{q}+} (\text{A}^{\text{n}-})_{\text{q/n} \cdot \text{y}} \text{H}_2\text{O}$, usual Z equal with 2 or 1 and M^{II} and M^{III} are divalent and trivalent cations (Mahjoubi et al., 2017; Song et al., 2012). In order to compensating of positive charge at interlayer anion ($\text{A}^{\text{n}-}$) is used and x is molar ratio $\text{M}(\text{III})/\text{M}(\text{III})+\text{M}(\text{II})$. They have the octahedral MO_6 layers, which are alike to the metal hydroxides(Khan et al., 2017).

Here in, we synthesis NiFeAl/LDHs by the co-precipitation method and thoroughly characterized via X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM). Then NiFeAl/LDHs used as an improvably electrocatalyst for oxygen

generation. Via the use of Al^{3+} at synthesis of ternary NiFeAl/LDHs, we can conclude that doping Al (III) ions in to NiFe-LDH significantly increased their electrochemical activity due to high crystallinity at NiFeAl/LDHs incompared to NiAl-LDH and NiFe-LDH.

Materials and method

Nickel nitrate hexhydrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], Aluminium nitrate nonahydrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and Iron (III) nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], the precursors for synthesis of ternary-component layer double hydroxide, were purchased from Merck Company (Germany) and used as received. Other chemicals were utilized without further purification.

X-ray diffraction (XRD) patterns were achieved on a Bruker AXS model D8 Advance diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at 40 kV. The size and morphology of the products were studied using a field-Emission scanning electron microscope (FE-SEM)(TE-SCAN) operating at 10 kV.

Results and Discussion

Characterisation of LDHs

XRD analysis

The XRD patterns of $\text{Ni}_2\text{Al-LDH}$, $\text{Ni}_2\text{Fe-LDH}$ and $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}\text{-LDH}$ (Fig.1 (a, b, c)) show the hydrotalcite-like distinctive structures (Hou et al., 2023). The peaks of (003), (006), (012), (015), (018) and (110) have $R\bar{3}m$ symmetry and hexagonal lattice structure (Ray et al., 2023).

The basal spacing (d_{003}) of the LDH was calculated to be 0.803, 0.773 and 0.764 nm at $2\theta = 11.5^\circ$ that show intercalation of CO_3^{2-} anions into the layer galleries at tree sample (Figure 1 (a, b and c)). The basal spacing (d) obtained from Braggs law, $n\lambda = 2d\sin(\theta)$ where $n=1$, λ is the wavelength of the incident light, and θ is the angle of incidence (Hunter et al., 2016; Xie & Liu, 2023). This show that in all three sample CO_3^{2-} ion intercalated into layers galleries between LDHs (Bhojaraj & Rajamathi, 2023; Qiu et al., 2022).

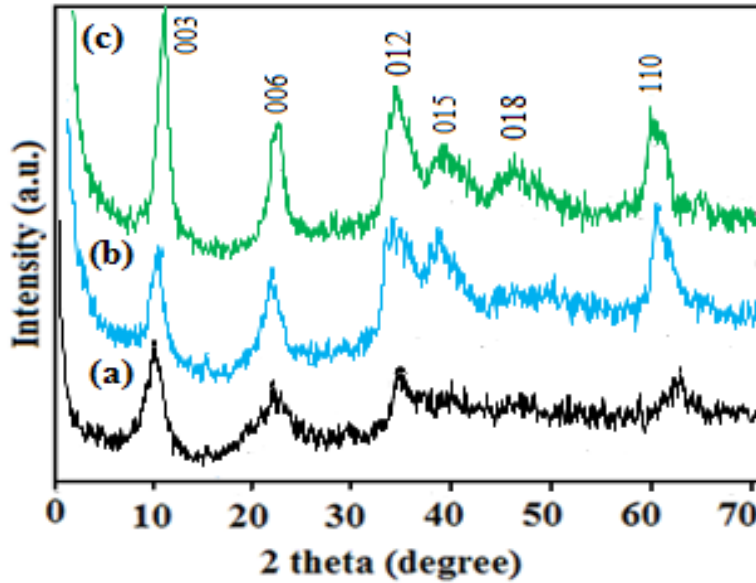


Figure 1. XRD spectra of (a) $\text{Ni}_2\text{Al-LDH}$, (b) $\text{Ni}_2\text{Fe-LDH}$ and (c) $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}\text{-LDH}$

The field-emission scanning electron microscopy (FE-SEM)

The size and morphology of the resulting material were characterized by FE-SEM image. (Figure 2 (a, b and c)) show the FE-SEM images of $\text{Ni}_2\text{Al-LDH}$, $\text{Ni}_2\text{Fe-LDH}$ and

$\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}\text{-LDH}$ which display a plate-like morphology and thickness of nanosheets are 11, 13 and 16 nm. Besides, the broad peaks at XRD pattern (Figure 2 (a, b and c)) confirms the nano structures in all three samples and increased size at $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}\text{-LDH}$.

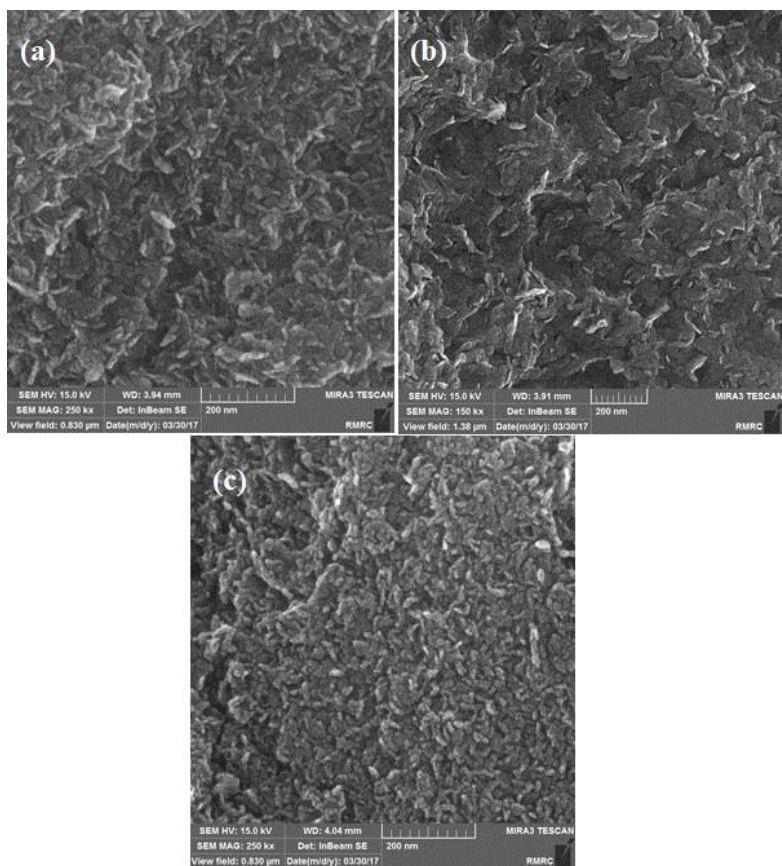


Figure 2. (a) FE-SEM images of a) $\text{Ni}_2\text{Al-LDH}$ b) $\text{Ni}_2\text{Fe-LDH}$ and c) $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}\text{-LDH}$

Electrochemical WOR measurements

Figure 3 (a) and (b) shows the linear sweep voltammetry (LSV) curves on a Saturated calomel electrode (SCE) scale. As show at Figure 3 (a) Bare electrode shows very poor OER activity with the need of large overpotential of 311mV to drive 0.7 mAcm^{-2} . $\text{Ni}_2\text{Fe-LDH}$ exhibits excellent activity and only demands overpotential of 81 mV to approach the same current density. $\text{Ni}_2\text{Al-LDH}$ is also active for OER but with the need of overpotential of 236 mV for 0.7 mAcm^{-2} .

In sharp contrast, $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}\text{-LDH}$ shows much superior OER activity over $\text{Ni}_3\text{Fe-LDH}$ and only demands much smaller overpotentials of 11mV to afford geometrical catalytic current densities of 0.7 mAcm^{-2} . As show at Figure 3 (a) the $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}\text{-LDH}$ in compared to $\text{Ni}_2\text{Al-LDH}$, $\text{Ni}_2\text{Fe-LDH}$, provided the earliest onset potential. The onset potential for $\text{Ni}_2\text{Al-LDH}$ and $\text{Ni}_2\text{Fe-LDH}$ is 1.15, 1.03 which are 0.17 and 0.05 V larger than $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}\text{-LDH}$. The onset potential of $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}\text{-LDH}$ is about 0.98V and indicating the start of water

oxidation. Despite the similar OER overpotentials of the three catalysts, the $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}$ -LDH can attain the highest current density at the same applied potential. This result underscores the importance of assembling catalytically active materials at the molecular level in designing high performing electrochemical catalysts.

Based on results obtained from Fig. 6 (b) doping 0.1 mol Al^{3+} and synthesis $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}$ -LDH suggested because $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}$ -LDH have lowest onset potential and highest current density. It is more favorable catalyst for OER.

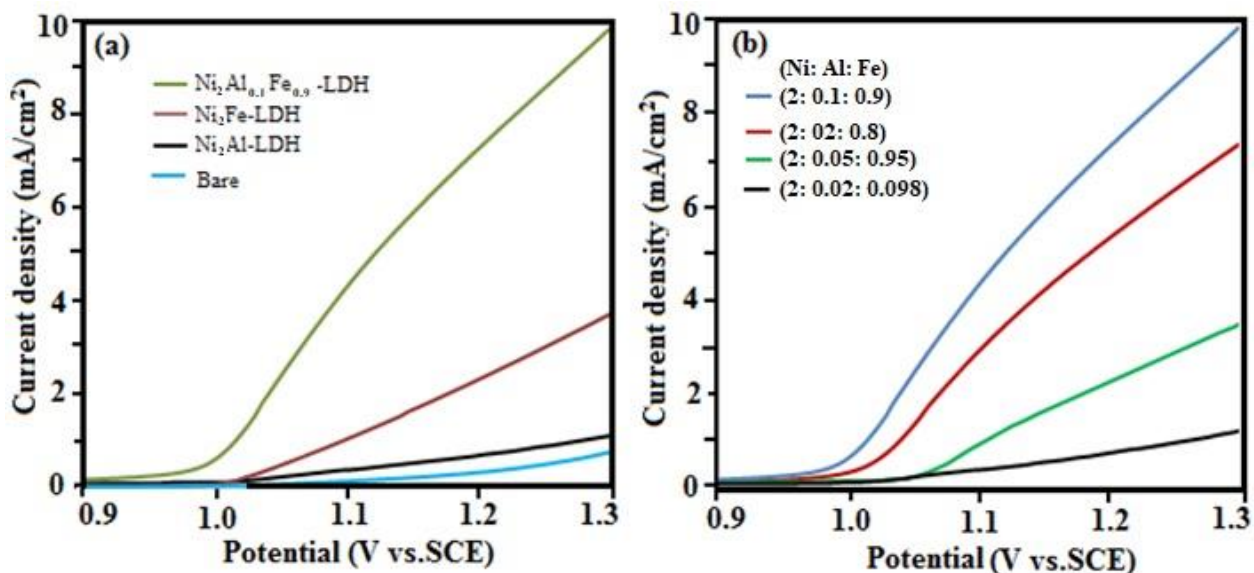


Figure 3. (a) Linear sweep voltammetric tests at neutral solution and using Ni_2Al -LDH, Ni_2Fe -LDH and $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}$ -LDH as electrocatalyst and (b) the effect amount of Al^{3+} doping into NiAlFe -LDH at OER

Conclusions

In summary, the $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}$ -LDH which synthesis by co-precipitation method is applied as a new low-overpotential catalyst for efficiently electrochemical water oxidation at neutral solutions. Electrochemical measurements have

demonstrated their excellent performance as OER electrocatalysts in neutral media. Linear sweep voltammetry measurements show that the $\text{Ni}_2\text{Al}_{0.1}\text{Fe}_{0.9}$ -LDH exhibited high-performance catalytic activity for electrochemical water oxidation in neutral solution, which are superior or comparable to those of Ni_2Al -LDH and Ni_2Fe -LDH with

similar structures in terms of the onset potential.

Acknowledgment

We are grateful to Azarbijan Shahid Madani University for financial supports.

References

[1] Omer, A.M.; *J. Renew. Sustain. Energy*. 2009, 5

[2] Wang, G.; Chang, J.; Tang, W.; Xie, W.; Ang, Y.S.; *J. Phys. D Appl. Phys.* 2022, 5, 293002.

[3] Quang, N.D.; Van, P.C.; Majumder, S.; Jeong, J.-R.; Kim, D.; Kim, C.; *J. Colloid Interface Sci.* 2022, 616,749

[4] Kubendhiran, S.; Chung, R.-J.; Yougbaré, S.; Lin, L.-Y.; Wu, Y.-F.; *Int. J. Hydrogen Energy*. 2023, 48, 101.

[5] Nai, J.; Yin, H.; You, T.; Zheng, L.; Zhang, J.; Wang, P.; Jin, Z.; Tian, Y.; Liu, J.; Tang, Z.; *Adv. Energy Mater.* 2015, 5, 1401880.

[6] Tang, D.; Han, Y.; Ji, W.; Qiao, S.; Zhou, X.; Liu, R.; Han, X.; Huang, H.; Liu, Y.; Kang, Z.; *Dalton Trans.* 2014, 43, 15119.

[7] Ping, J.; Wang, Y.; Lu, Q.; Chen, B.; Chen, J.; Huang, Y.; Ma, Q.; Tan, C.; Yang, J.; Cao, X.; *Adv. Mater.* 2016, 28, 764.

[8] Wang, Q.; O'Hare, D.; *Chem. Rev.* 2012, 112, 4124.

[9] Guo, X.; Zhang, F.; Evans, D.G.; Duan, X.; *ChemComm.* 2010, 46, 5197.

[10] Fan, G.; Li, F.; Evans, D.G.; Duan, X.; *Chem. Soc. Rev.* 2014, 43, 7040.

[11] Alcantara, A.; Aranda, P.; Darder, M.; Ruiz-Hitzky, E.; *J. Mater. Chem.* 2010, 42, 9495.

[12] Nayak, S.; Mohapatra, L.; Parida, K.; *J. Mater. Chem.* 2015, 3, 18622.

[13] Song, J.; Leng, M.; Fu, X.; Liu, J.; *J. Alloys Compd.* 2012, 543, 142.

[14] Mahjoubi, F.Z.; Khalidi, A.; Abdennouri, M.; Barka, N.; *J. Taibah Univ. SCI.* 2017, 11, 90.

[15] Khan, I.; Yamani, Z.H.; Qurashi, A.; *Ultrason. Sonochem.* 2017, 34, 484.

[16] Hou, L.; Zhou, X.; Kong, L.; Ma, Z.; Su, L.; Liu, Z.; Shao, G.; *Nanomater.* 2023, 13, 1192.

[17] Ray, P.K.; Mohanty, R.; Parida, K.; *J. Energy Storage.* 2023, 72, 108335.

[18] Xie, J.-J.; Liu, H.-W.; *Appl. Math. Model.* 2023, 119, 717.

[19] Hunter, B.M.; Hieringer, W.; Winkler, J.; Gray, H.; Müller, A.; *Energy Environ. Sci.* 2016, 6, 1734.

[20] Bhojaraj, M.; Rajamathi,; *ACS.* 2023, 10185.

[21] Qiu, Y.; Liu, Z.; Zhang, X.; Sun, A.; Liu, J.; *Appl. Surf. Sci.* 2022, 598, 153690.