

SYNTHESIS AND CHARACTERIZATION OF HIGH ENTROPY OXY-HYDROXIDES FOR ELECTROCATALYTIC OXYGEN EVOLUTION AND REDUCTION REACTIONS

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Keywords	Abstract
High entropy materials Water splitting	<i>The need for energy is rising quickly, and the usage of fossil fuels is contributing to the greenhouse effect and environmental pollution, both of which are raising public concerns. The development of novel electrochemical energy storage techniques as well as the creation of cleaner, more sustainable energies have both become highly researched topics as a result of this condition. New functional materials are being investigated for the advancement of energy storage. High entropy hydroxides have lately been emerged as promising electrocatalyst for universal water splitting reactions, which are central for solid oxide fuel cells, hydrogen production and metal-air batteries. In this work, a cost-effective and scalable fabrication method was applied to fabricate several high entropy hydroxides on Nickel foam through single-step electrodeposition technique. Results showed that high-entropy FeCoNiMnOOH exhibits excellent OER activity with a low overpotential of 151 mV at current density of 100 mA cm⁻², which is associated with the presence of defects in the structure.</i>

YÜKSEK ENTROPİLİ OKSİ-HİDROKSİTLERİN ÜRETİLMESİ, KARAKTERİZASYONU VE OKSİJEN ÇEVİRİM REAKSİYONU ELEKTRO KATALİZÖRÜ OLARAK UYGULANMASI

Anahtar Kelimeler	Öz
Yüksek entropili malzemeler Su ayrışma reaksiyonu	<i>Artan enerji talebini karşılamak ve çevre kirliliği endişelerini azaltmak için yenilenebilir enerji sistemleri ve verimli enerji dönüşüm cihazları kullanmak, yeni elektrokimyasal enerji depolama sistemleri geliştirmek gerekmektedir. Bu bağlamda, hidrojen üretimi, katı yakıt hücreleri ve metal-hava bataryaları gibi yeni nesil enerji üretme ve depolama sistemlerinde oksijen çevrim reaksiyonları sistemlerin performanslarında önemli rol oynamaktadır. Dolayısı ile bu reaksiyonları hızlandırmak için yeni fonksiyonel malzemeler araştırılmaktadır. Yüksek entropili hidroksitler, son zamanlarda, katı oksit yakıt hücreleri, hidrojen üretimi ve metal-hava pilleri için merkezi olan evrensel su ayırma reaksiyonları için umut verici bir elektrokatalizör malzemesi olarak ön plana çıkmıştır. Bu çalışmada, tek adımlı elektrodpozisyon tekniği ile Nikel köpük üzerinde farklı kompozisyonlarda yüksek entropili hidroksitler' in direkt üretimi araştırılmıştır. Elde edilen elektrokatalizörlerin elektrokimyasal performanslarına üretim voltajı, suresi ve elementel etki incelenmiştir. Sonuçlar, yüksek entropili FeCoNiMnOOH' un 100 mA cm⁻² lik akım yoğunluğunda 151 mV' lik düşük bir aşırı potansiyeli sergilediğini göstermiştir. FeCoNiMnOOH yüksek oksijen oluşum reaksiyonu katalitik aktivitesi ise yapıda bulunan oksijen hataları ile ilişkilendirilmiştir.</i>

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1. Introduction

Energy obtained from hydrogen has been foreseen to be the greenest way to meet the demand for carbon-free

society and to produce hydrogen, electrochemical water splitting has been noticed as the most feasible method. Electrochemical water splitting depends on two half-cell reactions, oxygen evolution reaction (OER) and oxygen



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reduction reaction (ORR), which have sluggish kinetics (Zhou et al., 2022). To mitigate the high overpotentials of these reactions, state-of-the-art electrocatalysts Pt/C, IrO₂, and, RuO₂ have been applied but they are scarce, expensive and also exhibit potential swings in a long term utilization (Wang et al., 2022). It is also not feasible to use two different catalysts to foster OER and ORR separately, since it would increase weight and cost in practical applications. Therefore, developing cost-effective and both structurally and electrochemically stable bifunctional oxygen electrocatalysts are essential to drive the cost down (Erdil et al., 2022).

Among the various approaches to design high performance bifunctional oxygen electrocatalysts, high-entropy effect driven based materials have been explored as a promising solution. High-entropy materials (HEMs) are single-phased materials that can consist of five or more metal cations in equimolar or near equimolar ratios (Rost et al., 2015). Mixed cationic sites of high entropy materials can interact with the intermediate species successfully; as a result, they may exhibit excellent catalytic activity (Bayraktar, Lökçü, Ozgur, Erdil and Toparli, 2022). HEMs can have various compositions, and they are tailorable; hence, their electrocatalytic activity can also be tuned.

2. Literature review

Several HEMs materials such as oxides, alloys, fluorides and sulfides have been explored and applied in numerous electrochemical applications. For example, it has been shown that high entropy fluorides exhibit a overpotential of 314 mV at a current density of 10 mA cm⁻² (Wang, Chen, Yang, Liang and Dai, 2020). High entropy MnFeCoNi HE alloys present OER overpotential of 302 mV at a current density of 10 mA cm⁻² (Dai, Lu and Pan, 2019).

One type of HEMs is high-entropy (oxy) hydroxides (HEHs) and they are considered to be a promising candidate as OER electrocatalysts. Yet, very few investigations have performed on quaternary or multinary (oxy)hydroxides, while most recent developments and discoveries have focused on pure binary (oxy) hydroxide materials and ternary (oxy)hydroxide composites. Typically, OER performance is can be enhanced via 3d-5d orbital repulsion and thus trimetallic (oxy)hydroxides are frequently combined with noble metal elements; nevertheless, this method is not economical.

FeCoNi hydroxide has been used as a quaternary material for OER after being doped with lanthanide. Due to their synergistic impact and electrical structure, most researchers believe that multimetal (oxy)hydroxides have outstanding water splitting properties (Liu et.al, 2020).

Another study demonstrated that the Fe element can modify the NiOOH electronic structure in NiFe-LDHs during the electrochemical reaction to enhance water

splitting (Trotochaud, Young, Ranney, and Boettcher, 2014).

The electronic structure of NiFeCo-LDH is modified and stabilized the Fe local environment in NiFe-LDHs to promote activity. Therefore, researching multi-metal (oxy)hydroxides in the water splitting reaction is a worthwhile endeavor.

Another critical issue in designing and application of electrocatalysts in water splitting is the contact between the catalysts and substrate. Typically, the catalysts are dropped on a substrate, but this method suffers from the conductivity. Therefore, it is crucial to grow the catalysts directly on a substrate to be used as working electrode.

In this work, for the first time we successfully grow three different high entropy hydroxides on a Nickel foam with a single step electrodeposition technique. The results show that increasing the deposition voltage increases OER activity due to higher surface coverage. On the other hand, substitution of Ni with Fe in the composition extremely enhances the OER performance which is attributed to the oxygen vacancy formation.

3. Method

In this study, research and publication ethics were complied with. High-entropy FeCoNiMnOOH and NiCoCrMnOOH powders were grown as in situ on Nickel foam through electrodeposition technique. Electrodeposition was carried out for different minutes at different voltages to investigate the time and voltage influence on the catalytic activity of samples. FeCoNiMnOOH and NiCoCrMnOOH were obtained on a Nickel foam. Co(NO₃)₂·3H₂O, Ni(NO₃)₂·6H₂O, Mn(NO₃)₂ and Fe(NO₃)₃·9H₂O as determined ratios were dissolved in ultrapure water to prepare the electrolyte solution for electrodeposition. The variations and compositions of catalysts on NF are; FeCoNiMnOOH (90 min, -1.5 V), FeCoNiMnOOH (60 min, -1.0 V), NiCoCrMnOOH (30 min, -1.5 V), NiCoCrMnOOH (60 min, -1.0 V), NiCoCrMnOOH (60 min, -2.0 V).

3.2. Characterization of High Entropy Oxy(Hydroxides)

The crystal structures of the series of FeCoNiMnOOH/NF and NiCoCrMnOOH/NF were studied by powder X-ray diffraction (XRD, Rigaku) with Cu K α radiation in a 2 θ range of 10–90°. Surface morphologies of the samples were investigated by SEM analysis. The SEM pictures of the synthetic high-entropy FeCoNiMnOOH/NF and NiCoCrMnOOH/NF at various magnifications are obtained. The chemical composition and nature of the high entropy hydroxides were studied using X-ray photoelectron spectroscopy with Al K α radiation. All the peaks were calibrated with standard C 1s spectrum at 284.6 eV.

3.3. Electrochemical tests

The electrochemical measurements were performed on a three-electrode system with a GAMRY Reference 3000 potentiostat/galvanostat/ZRA. Ag/AgCl electrode was used as a reference, and a platinum wire was used as a counter electrode. All tests were measured in an O₂ saturated solution of 0.1 M KOH prepared from deionized water and KOH pellets.

4. Results

The XRD patterns of electrodeposited Ni-foams and bare Ni-foam are provided in Figure 1.

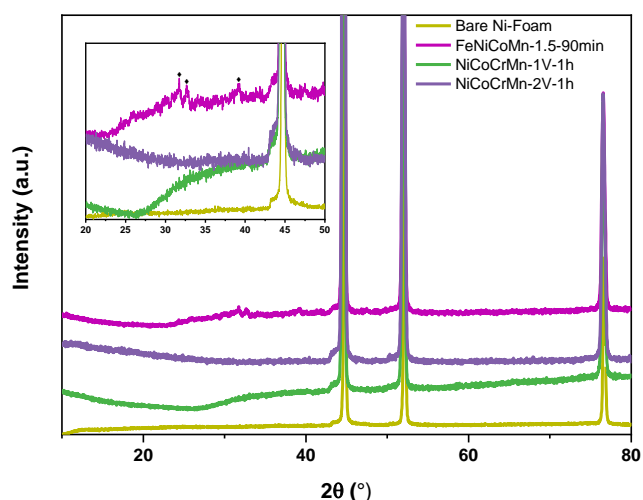


Figure 1. XRD spectra of Nickel foam, FeCoNiMnOOH and NiCoCrMn on Nickel foam.

The distinctive diffraction peaks of the Ni-foam at 44.3° , 51.8° , and 76.4° are represents the (111), (200) and (220) planes. The electrodeposited Ni-foams display amorphous nature as shown from the XRD graph. There is no obvious diffraction peak other than Ni-foam peaks. Only FeCoNiMn displays small diffraction peaks at 32° , 34° and 40° . These peaks can be corresponded to FeNiOOH peaks, such as $(\text{Fe}_{0.67}\text{Ni}_{0.33})\text{OOH}$, $(\text{Fe}_{0.67}\text{Mn}_{0.33})\text{OOH}$ and/or $(\text{Fe}_{0.67}\text{Co}_{0.33})\text{OOH}$. The others are display the typical amorphous XRD pattern. The extraordinary electrocatalytic performance of FeCoNiMn with respect to others can be also related to these crystalline (oxy)hydroxide peaks.

SEM images of bare Nickel foam and deposited FeNiCoMn and NiCoCrMn are shown in Figure 2. The images indicate that the foam was successfully coated with HEO-OH.

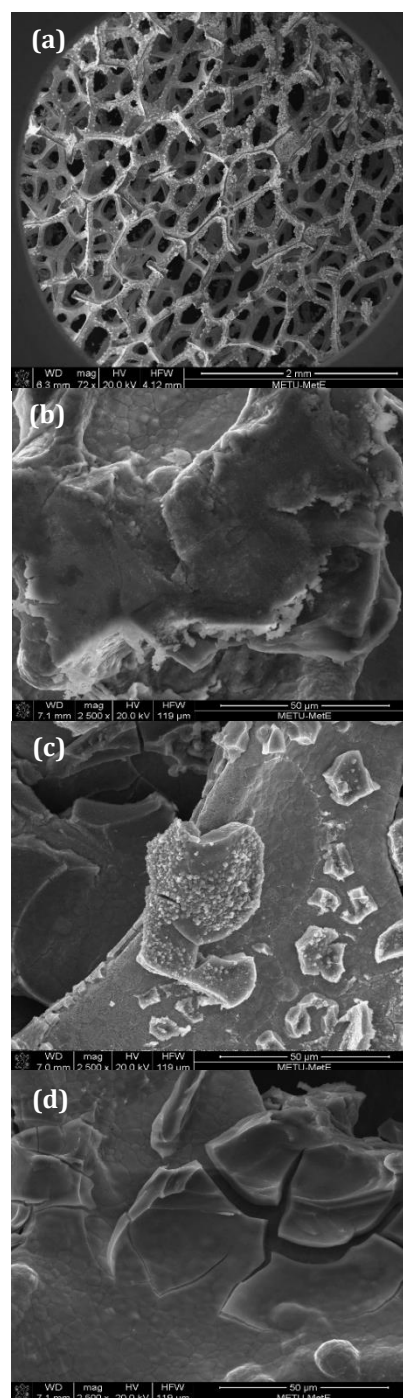


Figure 2. SEM image of a. the bare Nickel foam b. SEM image of the FeNiCoMn-1.5V-90 min c. SEM image of the NiCoCrMn-1.0 V-60 min d. SEM image of the NiCoCrMn-2.0V-60 min.

Figure 3 shows the XPS core level spectra of O1s from FeNiCoMn and NiCoCrMn samples.

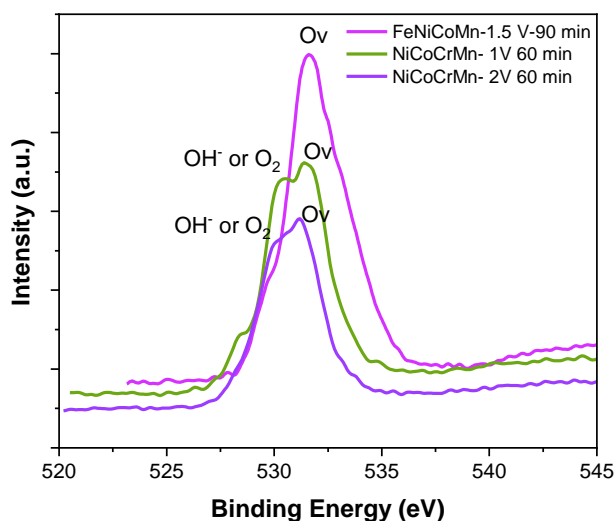


Figure 3 XPS core level spectra of O1s.

Here, it is clearly seen that the peak related to the oxygen vacancy formation at ~ 531 eV becomes more dominant in the spectra of FeNiCoMn deposited at -1.5 V during 90 min. (Lokcu, Toparli and Anik, 2020) Nickel, Cobalt, Chromium, Manganese, and Iron were electrodeposited to bare nickel foam with various voltages and time. Firstly, to investigate the OER performance of the electrocatalysts, linear sweep voltammetry (LSV) in 0.1 M potassium hydroxide (KOH) electrolyte was investigated with rotating disc electrode (RDE). During the experiments, Ag/AgCl reference electrode was used, then all the potential values were converted according to the reversible hydrogen electrode (RHE). After that, at $100 \text{ mA}\cdot\text{cm}^{-2}$ current density, the overpotential values, which shows us the electrocatalytic activity of the OER catalysts according to the literature, were measured for all the electrocatalysts. The overpotential values for cobalt, chromium, and manganese electrodeposited samples (NiCoCrMn) which, -1.0 V for 1 hour and -2.0 V for 1 hour were 725, and, 446 mV, respectively as shown in Figure 4.

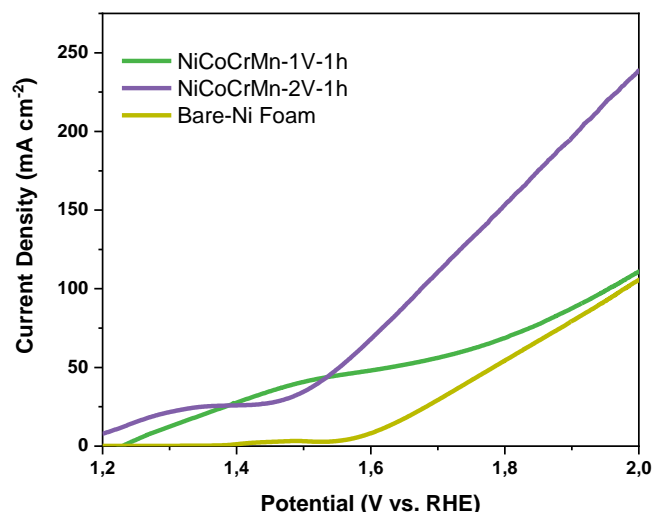


Figure 4. OER activity curves of NiCoCrMn on Nickel foam in 0.1 M KOH electrolyte.

Hence, NiCoCrMn produced with -2.0 V with 1 hour has the lowest overpotential. As compared to bare nickel foam with an overpotential of 750 mV, OER activity of electrodeposited sample were enhanced as shown in Figure 4. Moreover, when iron deposited on the nickel foam instead of chromium (FeNiCoMn), the overpotential value becomes 151 mV as shown on Figure 5. Hence, it can be concluded that iron increases the electrocatalytic OER activity significantly.

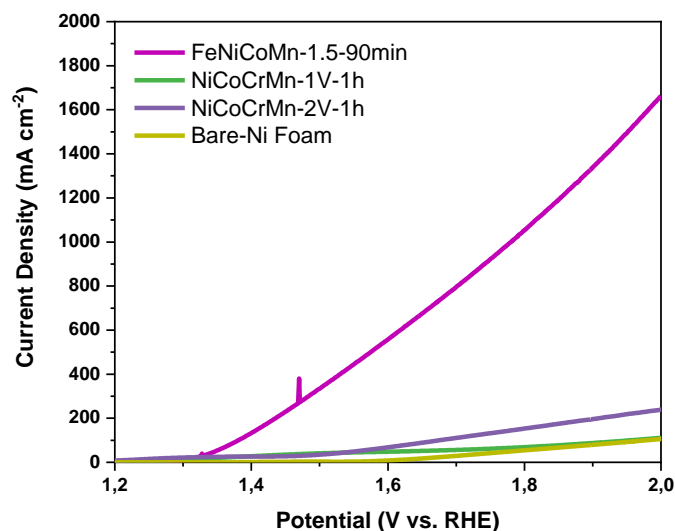


Figure 5. OER activity curves of FeNiCoMn and NiCoCrMn on Nickel foam in 0.1 M KOH electrolyte.

Figure 6 shows the Tafel plots which were obtained to understand the reaction kinetics of the electrocatalysts.

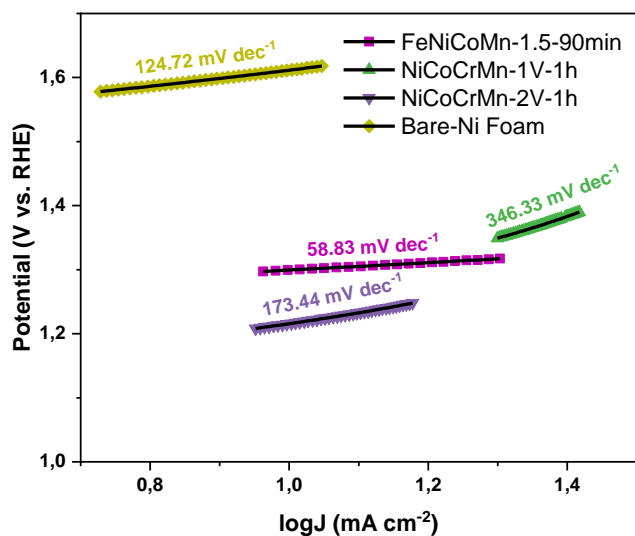


Figure 6. Tafel analysis of FeNiCoMn and NiCoCrMn on Nickel foam in 0.1 M KOH electrolyte.

Tafel slopes of NiCoCrMn produced under -1.0 V for 1 hour and -2.0 V for 1 hour were 346.33, and 173.44 $\text{mV}\cdot\text{dec}^{-1}$, respectively. Hence, NiCoCrMn produced with -2.0 V for 1 hour has the lowest Tafel slope which means that reaction kinetic is faster than the other samples. Hence, when cobalt, chromium, and manganese electrodeposited on the nickel foam at -2.0 V for 1 hour, OER activity is better than the other samples that are produced with various voltage and time. Additionally, iron deposited on nickel foam shows the lowest Tafel slope among the other electrocatalysts with a 58.83 $\text{mV}\cdot\text{dec}^{-1}$. Hence, deposition of iron instead of chromium promotes the reaction kinetics. As a result, FeNiCoMn produced at -1.5 V for 90 minutes has the best electrocatalytic OER activity with low overpotential and faster reaction kinetic among the other electrodeposited electrocatalysts. Since, iron deposited sample has the highest OER electrocatalytic activity, to understand its bifunctional activity the electrocatalytic oxygen reduction reaction (ORR) activity was measured with RDE in O_2 saturated 0.1 M KOH solution. Then, ORR activity of FeNiCoMn was compared with ORR activity of bare nickel foam as shown in Figure 7. At -1 mA/cm^2 current density, the potential was 1.04 V for FeNiCoMn. Hence, FeNiCoMn has better electrocatalytic ORR activity than bare nickel foam.

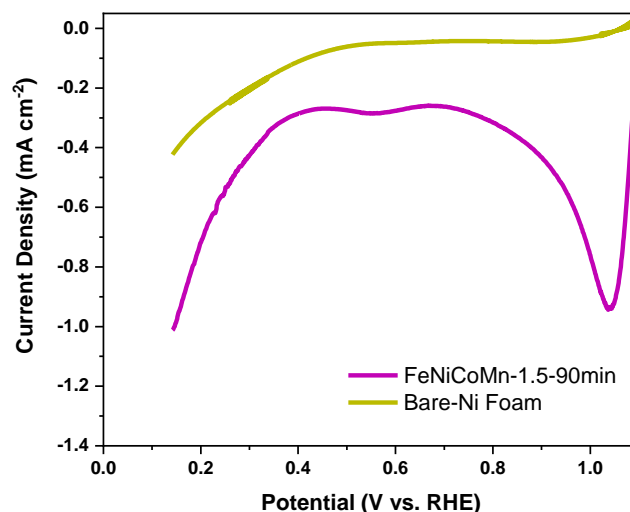
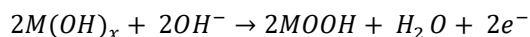
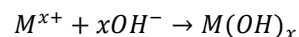
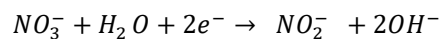


Figure 7. ORR activity curves of FeCoCrMn on Nickel foam in 0.1 M KOH electrolyte.

5. Discussion

Electrodeposition is a facile and fast technique of fabricating self-assembled oxyhydroxide electrocatalysts than the traditional wet chemistry methods. Therefore, electrodeposition technique holds a great potential to fabricate electrocatalysts directly on a gas diffusion layer. The reduction reaction of NO_3^- is driven by the electrodeposition with constant voltage, as shown in Eqs.



The production of the nanosheets was successful, according to SEM pictures. The SEM pictures of the synthetic high-entropy FeCoNiMnOOH/NF and NiCoCrMnOOH/NF at various magnifications are shown in Figure 2. The FeCoNiMnOOH and NiCoCrMnOOH nanosheets created small nano-nests and grew uniformly on the Nickel foam surface, which improved the capacity for gas spilling. These nanosheets also form a protective shell around one another with various angles and morphologies, increasing their surface area and exposing numerous active sites. Surface area and active sites were also increased by the twisted and uneven nanosheets. The OER performance benefits from the microstructure and morphology. When comparing the deposited surfaces, FeCoNiMnOOH with 90 min and -1.5 V shows the best deposited performance so that the bare Nickel foam under the deposit is not even seen. However, as the time and applied voltage decreases, the amount of the deposited material decreases accordingly.

Also, it can be observed that, when the formula is changed by replacing Fe with Cr, the deposited amount is decreased. The evidence of the deposited material are the crack formations and the bubble-like structure on

the foam structure. Table 1 compares the state-of-the-art electrocatalysts performance with this work.

Table 1. Literature Review Of State-Of-The-Art Electrocatalysts And Comparison With This Work

Electrocatalysts	Overpotential for OER (mV)	Overpotential for ORR (mV)
RuO ₂ Erdil et al., 2022	0.82	1.62
IrO ₂ Erdil et al., 2022	0.38	1.57
NiCoCrMn This work	0.44	-
FeNiCoMn This work	0.15	1.04

According to the LSV results, FeCoNiMnOOH/NF (90 min, -1.5 V) shows the highest electrocatalytic activity with the lowest overpotential. NiCoCrMnOOH/NF (60 min, -1.0 V) shows the lowest activity with the highest overpotential. Moreover, XPS O1s core level spectra of HEO-OH indicates that oxygen vacancy peak dominates the O1s core level spectra of FeCoNiMnOOH. Therefore, the higher OER activity of FeCoNiMnOOH can be associated with the defective structure, which is well aligned with the literature.

6. Conclusion

FeCoNiMnOOH and NiCoCrMnOOH were synthesized through one-step electrodeposition technique directly on a Nickel foam. Electrochemical OER test results represent that FeCoNiMnOOH has superior OER performance in 1 M KOH than the state-of-art electrocatalysts. The high OER performance of FeCoNiMnOOH is associated with moderate surface surface coverage and defective structure. Therefore, electrodeposition technique is foreseen to be facile approach for direct fabrication of HEHs on a substrate which also reduces contact problem and enhances charge transfer. Overall, synthesizing electrocatalyst via electrodeposition technique holds a great potential for industrial applications.

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Author Contributions

The author (Cigdem Toparli) is responsible for conceptualization, methodology, formal analysis, investigation and discussion of results, writing and reviewing of the manuscript.

Conflict of Interest

The author (Cigdem Toparli) has no conflicts of interest to disclose. This study complies with scientific research and publication ethics and principles.

References

- Bayraktar, O., Lökçü, E., Ozgur, C., Erdil, T. & Toparli, C. (2022). Effect of synthesis environment on the electrochemical properties of (FeMnCrCoZn)₃₀₄ high-entropy oxides for Li-ion batteries. *International Journal of Energy Research* 46, 22124–22133. doi: <https://doi.org/10.1002/er.8749>
- Dai, W., Lu, T. & Pan, Y. (2019). Novel and promising electrocatalyst for oxygen evolution reaction based on MnFeCoNi high entropy alloy. *Journal of Power Sources* 430, 104-111. doi: <https://doi.org/10.1016/j.jpowsour.2019.05.030>
- Erdil, E., Lökçü, E., Yildiz I., Okuyucu, C., Kalay, Y. E., Toparli, C. (2022). Facile Synthesis and Origin of Enhanced Electrochemical Oxygen Evolution Reaction Performance of 2H-Hexagonal Ba₂CoMnO_{6-δ} as a New Member in Double Perovskite Oxides. *ACS Omega* 7(48), 44147–44155. doi: <https://doi.org/10.1021/acsomega.2c05627>
- Liu, P. F., Yin, H., Fu, H.Q., Zu, M.Y., Yang, H.G., Zhao, H. (2020). Activation strategies of water-splitting electrocatalysts. *Journal of Materials Chemistry A* 8, 10096-10129. doi: <https://doi.org/10.1039/D0TA01680B>
- Lokcu, E. Toparli, C. & Anik, M. (2020). Electrochemical Performance of (MgCoNiZn)_{1-x}Li_xO High-Entropy Oxides in Lithium-Ion Batteries. *ACS Applied Materials Interfaces* 12 (21), 23860–23866. doi: <https://doi.org/10.1021/acscami.0c03562>
- Rost, C. M., Sachet, E., Borman, T., Moballeghe, A., Dickey, E. C., Hou, ... Maria, J. P. (2015). Entropy-Stabilized Oxides. *Nature Communications* 6 (1), 8485. doi: <https://doi.org/10.1038/ncomms9485>
- Trotochaud, L., Young, S. L., Ranney, J. K., & Boettcher, S. W. (2014). Nickel–Iron Oxyhydroxide Oxygen-Evolution Electrocatalysts: The Role of Intentional and Incidental Iron Incorporation. *Journal of American Chemical Society* 136 (18), 6744–6753. doi: <https://doi.org/10.1021/ja502379c>
- Wang, T., Chen, H., Yang, Z., Liang, J. & Dai, S. (2020). High-Entropy Perovskite Fluorides: A New Platform for Oxygen Evolution Catalysis. *Journal of American Chemical Society* 142 (10), 4550–4554. doi: <https://doi.org/10.1021/jacs.9b12377>
- Wang, Q., Li, J., Li, Y., Shao, G., Jia, Z., Shen, B. (2022). Non-Noble Metal-Based Amorphous High-Entropy Oxides as Efficient and Reliable Electrocatalysts for Oxygen Evolution Reaction. *Nano Research* 15, 8751–8759. doi: <https://doi.org/10.1007/s12274-022-4179-8>

Zhou, C., Chen, X., Liu, S., Han, Y., Meng, H., Jiang, Q., ...Zhang, R. (2022). Superdurable Bifunctional Oxygen Electrocatalyst for High-Performance Zinc-Air Batteries. *Journal of American Chemical Society* 144 (6), 2694-2704. doi: <https://doi.org/10.1021/jacs.1c11675>