

High-Entropy Alloys and Oxides as Supercapacitor Electrodes: A Structural and Electrochemical Perspective for Energy Storage

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This study investigates the performance of high entropy alloys [$\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV}$, HEA]] and high entropy oxides [$(\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV})\text{O}_4$, HEO]] as electrode materials for supercapacitors. HEA is synthesized through mechanical alloying, followed by HEO forming via an oxidation process. XRD results demonstrate HEA comprises both amorphous and crystalline phases, whereas HEO has an entirely crystalline structure. SEM analyses showed HEA exhibits larger and irregular particles, whereas HEO displays a smaller and spherical morphology. EPR analyses revealed significant changes in defect structures and unpaired electron configurations during the transition from HEA to HEO. HEA is prone to diffusion-controlled processes due to their regular structure and strong magnetic interactions; however, HEO exhibits capacitive behavior based on surface redox reactions and pseudo-capacitive mechanisms due to their irregular structure and oxygen vacancies. CV analyses revealed that HEO contributes more capacitive via surface redox reactions, while GCPL results suggested that HEO demonstrated superior energy density (40.8 Wh kg^{-1}) and power density (14.3 kW kg^{-1}). Impedance analyses revealed that HEO exhibited reduced internal resistance and enhanced ion conductivity, whereas HEA demonstrated higher resistance and diffusion-controlled processes. In conclusion, HEA and HEO exhibit distinct energy storage mechanisms, and these materials can be optimized for supercapacitor applications.

and engineering.^[1–3] High entropy alloys (HEA) and high entropy oxides (HEO) are the two types of this material class.^[1,2] These materials are particularly notable for their unique combination of mechanical strength, thermal stability, and chemical resistance, making them suitable for diverse applications.^[1–3] HEA, composed of five or more elements, forms a single-phase solid solution with exceptional mechanical strength, chemical stability, and thermal resistance.^[4,5] Upon oxidation, HEA transforms into HEO, which exhibits a disordered structure, enhanced surface redox reactions, and capacitive properties.^[4,5] HEA are widely preferred in aerospace, automotive, biomedical implants, and wear-resistant coatings due to their elevated strength, corrosion resistance, and thermal stability.^[6,7] HEO are used in catalysis, magnetic materials, sensors, and environmental applications, especially in fields where chemical stability and surface reactivity are essential.^[8,9] The different properties of these materials result from the high entropy of mixing and the interactions between elements facilitated by the combination of several metal ions within a single phase.

The change in composition between HEA and HEO results in significant changes to the material's structural, magnetic, and electrochemical properties.^[10,11] HEA are prone to

1. Introduction

High entropy materials have garnered significant interest in recent years due to their various applications in materials science

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diffusion-controlled processes because of their regular structure.^[12] In contrast, the disordered structure of HEO promotes surface redox reactions and improves energy storage performance via pseudo-capacitive mechanisms.^[10,11] These characteristics provide HEA and HEO intriguing to use as electrode materials in energy storage devices, particularly supercapacitors.^[13,14] Supercapacitors are energy storage devices characterized by high power density, extended cycle life, and rapid charge-discharge capabilities, with their performance significantly influenced by the electrode materials used.^[15,16] There are many studies in the literature on many different materials such as carbon materials, conductive polymers, transition metal/metal oxides, metal hydroxides, and nanocomposite materials for supercapacitor electrodes. These materials have advantages as well as disadvantages in electrode performance.^[17,18] For example, carbon-based electrodes provide high power density but have low specific capacitance and high cost;^[19,20] conductive polymers have good pseudocapacitive properties and electrical conductivity but poor stability during charge/discharge process;^[21–23] transition metals and metal oxides have higher theoretical specific capacitance ($100\text{--}2000\text{ F g}^{-1}$) and higher energy density than carbon materials (200 F g^{-1}) and better chemical stability than conductive polymers.^[24,25] Therefore, metal/metal oxides stand out in terms of these properties. However, despite extensive studies on heterogeneous single metal electrodes, shortcomings such as low reactivity, poor stability, and relatively slow electron transfer rate in the redox process generally limit the development of these catalysts.^[26,27] 3D transition metals are of increasing interest due to their rich earth resources and low cost, and their high entropy alloys and oxides have superior properties to traditional single metals and metal oxides.^[28] The advantages of HEA and HEO, such as having elemental diversity and high configurational entropy, forming solid solutions instead of intermetallic compounds, and therefore being more stable, cause them to have significantly higher chemical potential and different surface electronic properties compared to their traditional single/mixed metal counterparts.^[29,30] These materials contain different metal cations and interactions between different cations in their crystal structures, which leads to exciting, new, and unexpected functional properties.^[29] The entropy-balancing effect of compounds with high electron density increases charge storage capacity while improving cycling stability and other electrochemical properties.^[31] Talluri et al.^[31] synthesized the supercapacitor electrode material based on $(\text{CrMnFeCoNi})_3\text{O}_4$ nanoparticles with CrMnFeCoNi composition by reverse coprecipitation method. It was observed that it exhibited 239 F g^{-1} capacitance (2M KOH). In another study,^[32] high entropy perovskite oxide $\text{Sr}(\text{Zr}_{n-2}\text{Sn}_{n-2}\text{Hf}_{n-2}\text{Ti}_{n-2}\text{Nb}_{n-2})\text{O}_3$ (SZSHTN) was added to $\text{Na}_{n-5}\text{Bi}_{n-5}\text{TiO}_3$ (NBT) lead-free ferroelectric ceramics, which increased the high-temperature dielectric stability and energy storage performance. In a study using FeNiCoMnMg HEA nanoparticles as an electrode, a capacitance of 203 F g^{-1} (6M KOH),^[33] and in another study using $(\text{FeCoCrMnZn})_3\text{O}_4$ HEO as an electrode, a capacitance of 340.3 F g^{-1} (1M KOH) was found.^[34]

This work selected the transition metals Fe, Cr, Mn, Ni, and V for the synthesis of HEA and HEO due to their favorable redox behavior and their oxides' advantageous charge storage capabilities. In addition, the study conducted by Sarkar and col-

leagues stated that the use of “transition metals” (because of their tendency to form cations in a single-phase structure) is a critical method for use in electrode materials.^[35] The performances of $\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV}$ -HEA synthesized by the mechanical alloying method and $(\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV})\text{O}_4$ -HEO synthesized after an oxidation process at 1000°C (by incorporating more than one metal cation into a single-phase crystal structure) as supercapacitor electrode materials were investigated in detail. The electrochemical performances of HEA and HEO as supercapacitor electrode materials were compared. HEA is susceptible to diffusion-controlled processes owing to its regular structure and strong magnetic connections. In contrast, HEO shows capacitive behavior owing to surface redox reactions resulting from its irregular structure. Moreover, the interactions between HEO and different metal cations form a significant characteristic of the electrode material.

This study provides a perspective by comparing high-entropy materials' alloy and oxide forms, which have recently gained attention for their unique properties and potential applications in energy storage. Unlike most studies that utilize three-electrode systems for supercapacitor evaluations, this work employs a two-electrode system, addressing the gap in real-world application results and providing more practical insights. The transition between HEA and HEO was also examined in detail using Electron Paramagnetic Resonance (EPR) analysis, revealing changes in defect structures and unpaired electron configurations. These structural changes were further correlated with their effects on electrochemical parameters, offering a deeper understanding of the relationship between material structure and performance.

2. Experimental Section

2.1. The Synthesis of High Entropy Alloys and Oxides

This work produced $\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV}$ (HEA) and $(\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV})\text{O}_4$ (HEO) using supercapacitor electrode materials. As part of this objective, HEA was first produced using the mechanical alloying (MA) technique. HEO was subsequently produced using the oxidation of synthesized HEA. The elements utilized in the initial stage were measured in appropriate molar ratios. Table S1 (Supporting Information) displays the purity of the product and brand. The initial powder mixture that had not been processed at this stage was referred to as RAW. RAW was employed as a reference value for comparison in particular calculations. The RAW was then placed in a steel vessel with a capacity of 80 mL for the mechanical alloying (MA) process. MA under an argon atmosphere was conducted using a planetary high-energy ball mill (Retsch PM 100) for 60 h. The MA process was performed at 400 rpm with a hardened steel ball-to-powder ratio of 20:1. The grinding device stopped for 15 min following every 30 min of operation. This aims to enhance efficiency and reduce heating in the grinding bowl. Following the production of the HEA, the next stage starts to produce the HEO. During the second stage, the alloy powders underwent oxidation at 1000°C in an air atmosphere for 12 h. Following the oxidation process, the powders undergo milling at 400 rpm for a duration similar to that of the oxidation. **Figure 1** visually illustrates the production method.

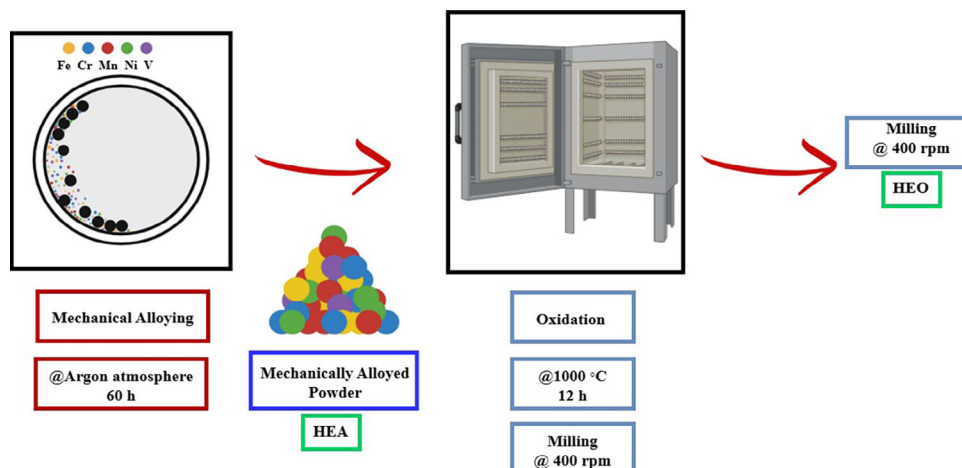


Figure 1. Flow chart of the synthesized HEA and HEO samples.

2.2. Thermodynamic Aspects of HEA as Starting Materials for HEO

Thermodynamic calculations were crucial for assessing the efficiency of synthesis methods, including MA and oxidation, in producing HEA and HEO.^[36] The enthalpy and entropy values derived from the HEA's thermodynamic calculations were used to classify alloys, an essential process. HEA was characterized by five or more elements and was defined as a solid solution.^[29] HEA was utilized in thermodynamic calculations as it functions as the initial alloy for HEO. The entropy of mixing (ΔS_{mix}) for HEA is represented by Equation 1:

$$\Delta S_{\text{mix}} = -R \sum_{i=1}^n c_i \ln c_i \quad (1)$$

In Equation 2, R is the gas constant ($8.314 \text{ J mol}^{-1} \cdot \text{K}$), c_i is the atomic ratio (mole fraction) of each component in HEA, and n is the total number of elements of the alloy. The enthalpy of mixing of the solid solution can be determined according to the ordered melt model.

$$\Delta H_{\text{mix}} = -R \sum_{i=1, i \neq j}^n \Omega_{ij} c_i c_j \quad (2)$$

Here, $\Omega_{ij} (= 4\Delta H_{AB}^{\text{mix}})$ is the regular melt interaction parameter between elements i and j , c_i is the atomic percentage of the i^{th} component, and $\Delta H_{AB}^{\text{mix}}$ is the enthalpy of mixing of the binary liquid alloy.^[37] The value was calculated using the Miedema model for atom pairs in the $\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV}$ [HEA]. **Table 1** shows the atom pair values between the elements Fe, Cr, Mn, Ni, and V determined by the Miedema model for the mixing enthalpy calculation.

Single-phase solid solutions in HEA were formed due to the high entropy of the mixing effect. The high entropy effect cannot solely solve the formation of intermetallic phases in HEA. Consequently, the Hume-Rothery rules, which consider valence electron concentration (VEC), electronegativity, and atomic size difference (δ), were crucial for the design and synthesis of HEA.

In this context, Ω denotes the ratio of mixing entropy to mixing enthalpy, as calculated by Equation 3, provided below.^[38]

$$\Omega = \frac{T_m \Delta S_{\text{mix}}}{\Delta H_{\text{mix}}} \quad (3)$$

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (4)$$

$$\varepsilon = [\beta - (K \lambda / D \cos \theta)] / 4 \tan \theta \quad (5)$$

Crystal sizes were calculated for RAW and HEO samples using the Scherrer equation^[39] in Equation 4. Here, D is the crystallite size, K is a constant ($K = 0.89$), λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the diffraction peak, θ is the diffraction angle, and ε is the microstrain.^[40] The lattice strain values of the samples were calculated using the Williamson-Hall (W-H) method by considering peak broadening as a function of 2θ to obtain size and strain broadening given in Equation 5.^[41]

2.3. Characterization Studies of HEA and HEO

The powders obtained were subjected to Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analyses. Characterization studies of the high entropy alloys produced after the MA process were carried out by XRD (X-Ray Rigaku Miniflex 600) using $\text{Cu-K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation

Table 1. Values of atom pairs between the elements Fe, Cr, Mn, Ni, and V are determined by the Miedema model for the ΔH mixing enthalpy calculation.

	Fe	Cr	Mn	Ni	V
Fe	Fe				
Cr	−1	Cr			
Mn	0	2	Mn		
Ni	−2	−7	−8	Ni	
V	−7	−2	−1	−18	V

Table 2. The specific supercapacitor designs are based on the synthesized nanocomposites.

Sample	Electrode 1	Electrode 2	Electrolyte	Separator	Type
HEA	HEA	HEA	6 M KOH	Glass fiber	Symmetric
HEO	HEO	HEO	6 M KOH	Glass fiber	Symmetric

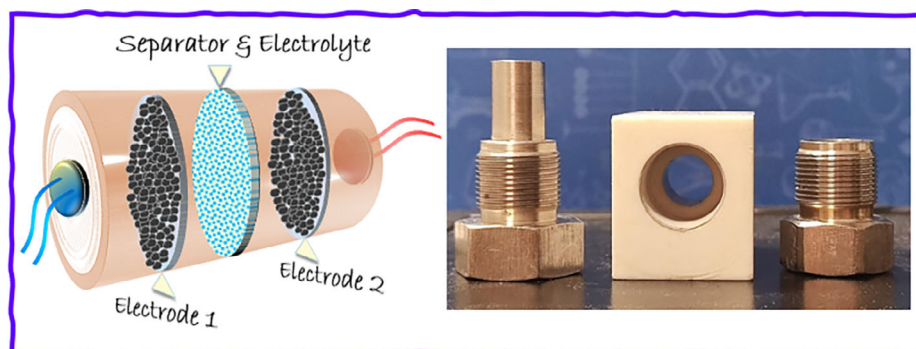
generated at 40 kV and 35 mA. The diffraction angle (2θ) varied from 10° to 90° with a step size of 0.02° . SEM evaluated the microstructural morphology of alloys and oxide at 5 kV (SEM; Hitachi SU3500) equipped with EDX (Oxford AZtech). XPS (Specs-Flex) analysis using Al-K α radiation to characterize the oxides formed (HEO) analyses. Bruker Benchtop EMX Nano EPR spectrometer with an integrated reference system for g-factor calculation and a spin counting unit performed EPR studies. The EPR spectra were obtained at room temperature using a 9.63 GHz resonator, 2 mW microwave power, and 2 G and 100 kHz modulation frequency and amplitude, respectively.

2.3.1. Electrochemical Characteristics and Supercapacitor Performances of HEA and HEO

Several analytical approaches, including potential electrochemical impedance spectroscopy (PEIS), cyclic voltammetry (CV), and galvanostatic charge/discharge (GCPL), were examined for supercapacitor performance using a VSM 300 BioLogic potentiostat. The produced HEA and HEO components were utilized in the fabrication of electrodes. The electrolyte used for the studies was 6 M KOH, with a 0–1 V voltage range. The impedance of the supercapacitors was assessed over a broad frequency range from 1 to 10 MHz. The investigation focused on high and low scanning rates and a broad scanning rate range of 1–200 mV s $^{-1}$ in the context of CV. The GCPL test assessed current densities ranging from 0.1 to 2.4 A g $^{-1}$. The content of the fabricated symmetric supercapacitor design and two-electrode setup are given in Table 2 and Scheme 1, respectively.

The energy density and power density of the manufactured electrodes have been determined using Equations 6 and 7, respectively. Here, ΔV (V) is the maximum potential window and Δt (s) is the discharging time.

$$\text{Specific Capacitance } (C_s) = \frac{\int_{V_1}^{V_2} I(V) dV}{2mV\Delta V} \quad (6)$$



Scheme 1. Represent schematic illustration and two-electrode system measurement of the supercapacitor device.

$$\text{Energy Density, } E = \frac{0.5 * C_s * \Delta V^2}{3.6} \quad (7)$$

$$\text{Power Density, } P = \frac{E}{(\Delta t/3600)} \quad (8)$$

Supercapacitor Fabrication: The electrochemical performance of high entropy composite materials, produced in alloy and oxide forms, was evaluated using two-electrode supercapacitor devices as electrode materials. A slurry was specifically formulated to prepare the working electrode. Carbon black (N330) and polyvinylidene fluoride (PVDF) serve as the active electrode materials for the slurry, having been ground together in a mortar at an 8:1:1 weight ratio for 10 min. 2 mL of N-methyl-2-pyrrolidone (NMP) were added, and the mixture was sonicated for an additional 30 min to achieve a homogeneous slurry. The formulation aims to reach a total solid mass of 100 mg. For coating applications, the surface of the stainless-steel current collector depicted in Scheme 1 is treated with $\approx 50 \mu\text{L}$ of the generated slurry solution. The functioning electrode was subsequently placed in an 80 °C vacuum oven overnight. The mass of the electrode material on the current collector was determined before and during the drying process. A round glass microfiber filter was positioned between two stainless steel screws, serving as a separator. $\approx 30 \mu\text{L}$ of electrolyte was applied to the filter, which was subsequently secured and tightened between the screws. The electrolyte consisted of a 6 M KOH solution, and the electrochemical characterization was conducted within the voltage range of 0–1 V.

Dunn's Method: The electrochemical performance of the symmetric device constructed with HEA and HEO composites has been additionally analyzed using the power law methodology.^[42,43] In the analysis, CV tests were conducted at scan rates of 1, 3, 5, 7, and 10 mV s $^{-1}$. The scan rate was determined by factors including minimal ohmic resistance and inductance and the optimal electrochemical properties observed in earlier studies. The power law (Eq. 9) can be articulated in the following manner:^[42,43]

$$i(v) = av^b \quad (9)$$

where i represents the current density (A/g), v denotes the scan rate (mV/s), and b was a constant. The value of b plays a crucial role in determining the charge storage mechanism of the device: b value closer to 1 signifies behavior characteristic of an electric double-layer capacitor (EDLC), where a charge was stored

Table 3. Thermodynamic calculations of the $\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV}$ -HEA sample.

ΔS_{mix}	ΔH_{mix}	ΔS_{conf}	Ω	δ %
12,51 J/(mol.K)	$-3.48 \text{ kJ mol}^{-1}$	1.51	6.74	3.44

electrochemically through the reversible adsorption of ions in the electrolyte, while b value closer to 0.5 indicates battery-like behavior, where a charge was stored via a redox reaction.^[44,45] The value of b can be calculated by taking the logarithm of Equation 10 as shown below:

$$\log(i(v)) = \log(k) + b \log(v) \quad (10)$$

3. Results and Discussions

3.1. Structural Properties

The thermodynamic calculations reveal that the $\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV}$ -HEA satisfies the conditions for forming a stable solid solution, with $\Omega = 6.74$ (>1.1) and $\delta = 3.44$ (<6.6), indicating strong entropy-driven stabilization and structural homogeneity.^[46] The results derived from thermodynamic calculations based on the equations are presented in Table 3. This high Ω value suggests a strong entropy-driven stabilization effect, which is critical for suppressing the formation of intermetallic phases. The δ value, well below the threshold of 6.6, further supports the structural homogeneity of the alloy. This demonstrates that the designed alloy conforms to the required conditions for forming a solid solution associated with the 2θ crystalline peak at 44° .

The value of ΔS_{conf} is crucial to evaluating the stability of the phase.^[47] The classification of an alloy as HEA is commonly recognized to occur when the criteria $\Delta S_{\text{conf}} \geq 1.5 R$ meet the criteria.^[48] According to Table 3, the ΔS_{conf} value of HEA is 1.51. Based on this result, it can be concluded that the alloy formed belongs to the HEA class.^[49]

Figure 2 presents the phases formed in the HEA, the powder mixture before the MA process (RAW), and HEO samples, as analyzed using the XRD technique. The XRD graph of the HEA presented in Figure 2a indicates the formation of crystalline and amorphous phases within the structure. Several parameters, including crystallite size, influence the shape of the diffraction peak. With a reduction in crystallite size, the diffraction peaks exhibit broadening. As the crystallite size diminishes, the crystal diffraction peaks can combine and broaden, resulting in a single broad diffraction peak, commonly referred to as a halo.^[38] If small amounts of crystalline phases exist in the structure, weak crystalline peaks may overlap with the amorphous peak, resulting in a single broad peak. A comparable situation is observed in the XRD graph presented in Figure 2a. The XRD patterns reveal a clear transition from a mixed amorphous-crystalline structure in the HEA sample to a fully crystalline structure in the HEO sample after oxidation. The broad diffraction peaks in the HEA sample suggest nanoscale crystallites, likely formed due to the prolonged MA process. In contrast, the sharp peaks in the HEO sample indicate improved crystallinity, which is consistent with the structural reorganization observed during the high-temperature oxidation process. This situation is believed to result from applying the

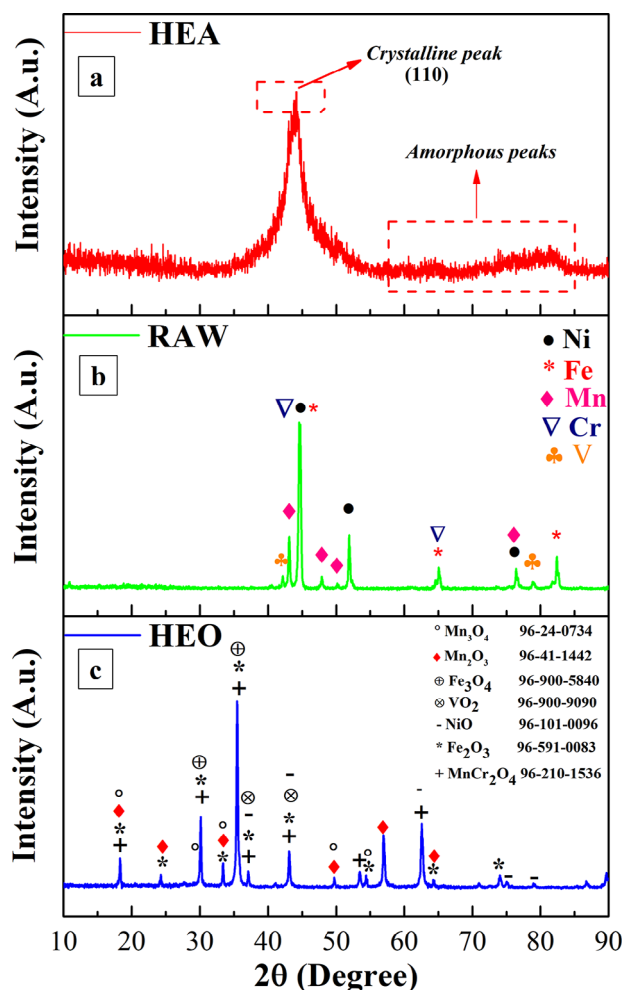


Figure 2. XRD patterns of the HEA, RAW, and HEO samples.

60 h MA process to the HEA sample. During the MA process, the repetitive welding-breaking-welding cycle reduces and reshapes particle size,^[50] forming both amorphous and crystalline phases within the structure. Figure 2b presents the XRD spectrum of the powder mixture, RAW, before MA, revealing characteristic diffraction peaks corresponding to Fe, Cr, Mn, Ni, and V. The XRD results of HEO presented in Figure 2c indicate that the amorphous structures observed in the HEA sample have fully crystallized due to oxidation. Different reagents exhibit distinct crystal structures.^[51] During the oxidation process of the HEA sample at 1000°C , the chemical formula is observed to be A_3O_4 ($(\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV})_3\text{O}_4$) for HEO, and the crystal structure transitions to the $\text{Fd}\bar{3}\text{m}$ structure due to the interactions among the components. The graph indicates the JCPDS numbers of the oxide structures corresponding to the 2θ peaks. The absence of vanadium oxide peaks in the XRD pattern of the HEO sample suggests that vanadium oxidation is primarily confined to the surface, as supported by the EDS and XPS analyses. This surface oxidation may contribute to the enhanced pseudo-capacitive behavior of the HEO material. The phase ratio of the oxide structures resulting from the HEO oxidation process was determined using the Rietveld Refinement technique with the Match Program, and

Table 4. Rietveld refinement result of Fe₃Cr₃Mn₂NiV-HEA and RAW sample.

Element	Phase Ratio [From XRD] %	Symmetry
V	0.8	Im-3m
Cr	13.9	Im-3m
Mn	19.7	I-43m
Fe	29.7	Im-3m
Ni	36	Fm-3m

the findings are presented in **Table 4**. The phase ratios obtained from the Rietveld refinement highlight the dominance of Fe and Ni phases in the HEA structure, with Fe contributing 29.7% and Ni contributing 36%. This suggests that these elements significantly stabilize the alloy's structure and influence its mechanical and electrochemical properties. The lower phase ratio of V (0.8%) may indicate its preferential oxidation during the synthesis process, as supported by the EDS results. Furthermore, the crystallite size of the HEO sample (52.852 nm) is significantly larger than that of the RAW sample (43.228 nm), indicating that the oxidation process promotes grain growth and structural reorganization (refer to **Table 5**). The lower dislocation density ($0.3579 \times 10^{-3} \text{ nm}^{-2}$) and higher macrostrain (0.001180) in the HEO sample suggest improved crystallinity and reduced structural defects, critical for enhancing ion mobility and surface redox reactions.

Microstructure images for HEA and HEO samples are given in **Figures 3** and **4**, respectively. According to the SEM images for the HEA sample in **Figure 3**, it is seen that the powder particles originating from the MA process have flattened and changed shape and have larger particles compared to the SEM images given for HEO. The larger and irregular particle morphology of HEA, as observed in SEM, aligns with the mixed amorphous-crystalline structure revealed by XRD, contributing to its diffusion-controlled processes. This phenomenon has been reported in similar studies.^[52,53] HEA's flattened and irregular particle morphology, resulting from the mechanical alloying process, may limit ion mobility and contribute to the dominance of diffusion-controlled processes in its energy storage mechanism. This structural characteristic aligns with HEA's higher charge transfer resistance during impedance analysis. As a result of the oxidation process, it is seen that HEO turns into a smaller particle size and a more spherical form. Additionally, as seen in the marked region in the SEM image in **Figure 4**, porosity is observed in some areas of the structure. The porosity observed in the HEO structure, as seen in **Figure 4**, can enhance the material's electrochemical performance by increasing the active surface area available for redox reactions. This porosity is a critical factor contributing to the pseudo-capacitive behavior of HEO, as it facilitates ion transport and surface redox reactions. As seen in the table of EDS results for HEA, the atomic percentage distribution is partially

Table 5. Structural parameters of synthesized HEO and RAW samples.

Sample	Crystallite size [nm]	Macrostrain [ε]	Dislocation density δ [10^{-3} nm^{-2}]
HEO	52.852	0.001180	0.3579
RAW	43.228	0.000186	0.5351

as expected. Fe 30%, Cr 30%, and Mn 20% are close to the expected values. However, contrary to expectations, Ni and V are below 10%. The oxidation affinities of the elements in the high entropy alloy (according to the formation free energy ΔG° values of the oxides in the Ellingham diagram) can be listed as V, Mn, Cr, Fe, and Ni, respectively. According to this order, element V forms a stronger bond with oxygen and is oxidized more easily. Therefore, when the EDS results for HEO are examined, it is seen that the vanadium element increases while the percentages of other elements mainly decrease.

The XPS analysis provides critical insights into the surface properties and oxidation states of the elements in HEO, which are directly related to its electrochemical performance. The deconvoluted XPS spectra for Fe 2p, Cr 2p, Mn 2p, Ni 2p, V 2p, and O 1s are presented in **Figure 5**. The analysis highlights the oxidation states of the elements and their contributions to the pseudo-capacitive behavior of HEO. The Fe 2p spectrum (**Figure 5a**) shows peaks at binding energies of 711.45 and 724.8 eV, corresponding to the Fe2p_{3/2} and Fe2p_{1/2} orbitals, respectively. Additional peaks at 709.5 and 710.9 eV indicate the Fe²⁺ oxidation state, while the peak at 713.01 eV corresponds to Fe³⁺. These results confirm the presence of Fe₂O₃ and Fe₃O₄ components, which contribute to the redox activity of the material.^[54,55] The Cr2p spectrum (**Figure 5b**) reveals peaks at 576.83 and 586.59 eV, corresponding to Cr2p_{3/2} and Cr2p_{1/2} orbitals of Cr⁴⁺. Additional peaks at 578.01 and 586.62 eV represent Cr³⁺ oxidation states. These findings indicate the coexistence of multiple oxidation states, which enhance the material's pseudo-capacitive behavior.^[56] The Mn2p spectrum (**Figure 5c**) shows peaks at 641.97 and 653.54 eV, corresponding to Mn2p_{3/2} and Mn2p_{1/2} orbitals of Mn³⁺. The fitting process for Mn2p is complex due to multiplet splitting and the interaction of d-electrons with valence band holes, which results in additional peaks. This complexity reflects the material's structural heterogeneity and its ability to support redox reactions.^[57,58] The Ni2p spectrum (**Figure 5d**) displays peaks at 856.14 and 873.19 eV, corresponding to Ni2p_{3/2} and Ni2p_{1/2} orbitals. Peaks at 855.34 and 856.8 eV indicate the presence of Ni²⁺ and Ni³⁺ oxidation states, respectively. Shake-up satellite peaks at 861.21 and 873 eV further confirm the presence of Ni in multiple oxidation states, which enhances the material's redox activity.^[59] The V2p spectrum (**Figure 5e**) shows peaks at 516.57 and 530.21 eV, corresponding to V2p_{3/2} and O1s orbitals. Peaks at 516.11 and 517.48 eV indicate the V⁵⁺ oxidation state. The O1s spectrum (**Figure 5f**) reveals three distinct peaks: O_I at 530.16 eV (surface lattice oxygen, O²⁻), O_{II} at 531.3 eV (oxygen vacancies or defects), and O_{III} at 532.63 eV (adsorbed oxygen species). The high oxygen concentration and the presence of oxygen vacancies are critical for enhancing pseudo-capacitive behavior and surface redox reactions.^[60-63] The absence of vanadium oxide peaks in the XRD pattern (**Figure 2**) suggests that oxidation occurs primarily on the surface. The presence of oxygen vacancies, as revealed by the O1s spectrum, plays a significant role in facilitating redox reactions and improving the electrochemical performance of HEO.

EPR analysis provides vital knowledge about the magnetic properties and structural configurations of HEA and HEO materials, and the obtained EPR spectra of produced samples are given in **Figure 6**.^[64] The analysis results demonstrate that the

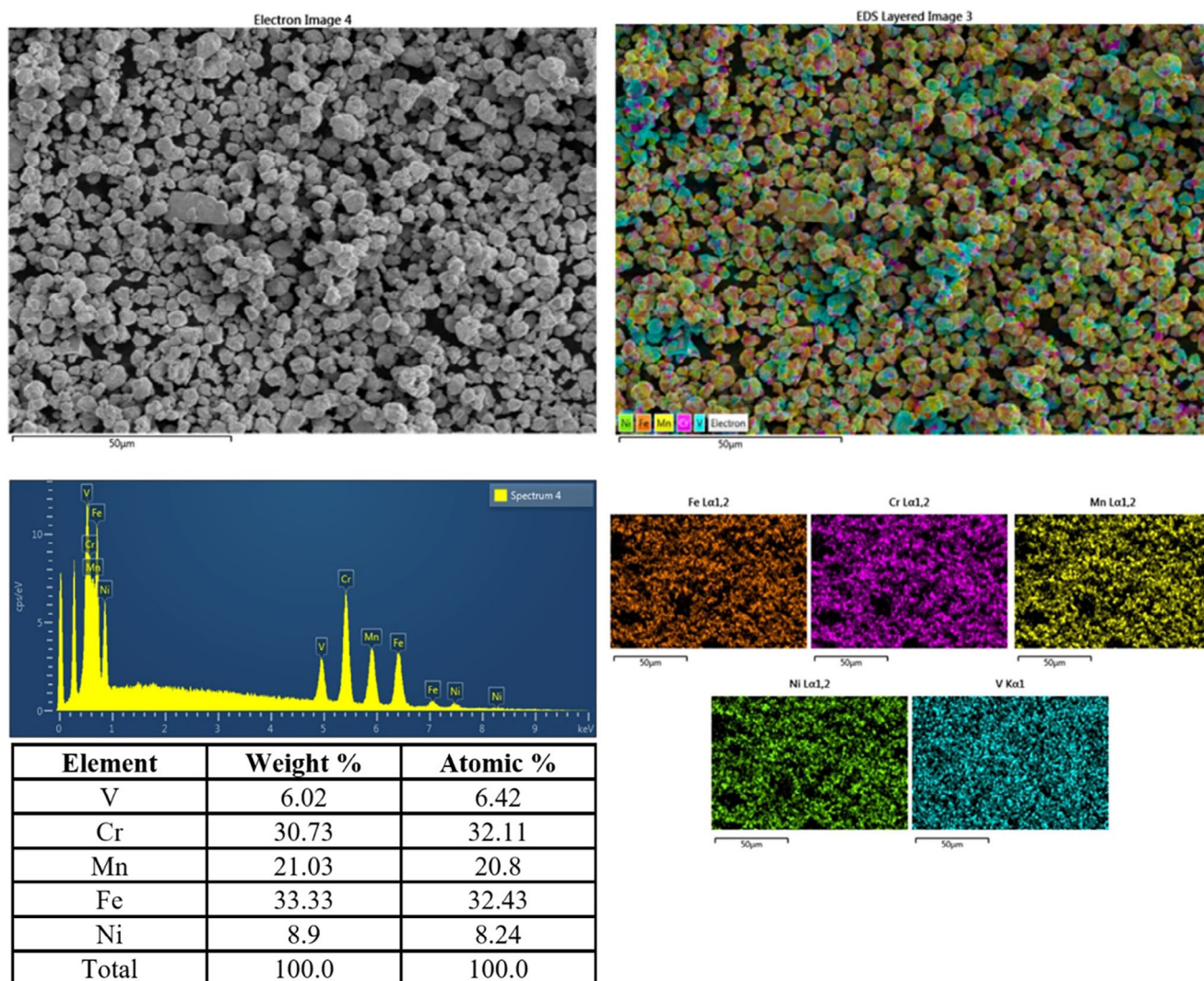


Figure 3. EDX images of the $\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV}$ -HEA sample.

g-factors for HEA and HEO materials were determined to be 2.08609 and 2.25916, respectively. These values indicate that both materials display paramagnetic properties, suggesting the presence of paramagnetic centers such as free radicals or transition metal ions within their structures, depending on the deviation of g-factors from $g \approx 2$.^[65] The EPR spectrum of HEA exhibits a sharper resonance signal and lower g-factor, indicating a more isotropic structure and reduced spin-spin interactions. This regularity in the structure of HEA reassures us about the predictability of their behavior and highlights the predominance of diffusion-controlled processes in their energy storage mechanism. A higher g-factor and a broader resonance signal were observed in the HEO material. A higher g-factor shows a strong crystal field effect within the material and a less regular alignment of spins.^[66] The broad signal width reflects the structural heterogeneity of HEO and the complexity of spin-spin interactions. This can be regarded as a characteristic that enhances the tendency of HEO to facilitate redox reactions and exhibit pseudo-capacitive behavior. The disparities observed in the EPR spec-

tra of HEA and HEO materials indicate fundamental differences in their energy storage mechanisms. HEA are more susceptible to diffusion-controlled processes due to their regular structure and strong magnetic interactions. In contrast, HEO demonstrates a mechanism primarily influenced by capacitive behavior, attributed to their disordered structure and propensity for surface redox reactions. The results represent that both materials can be optimized for various energy storage applications and possess significant potential. As a result, in both samples, spin-spin exchange, or dipolar coupling, is causing a broadening in the EPR signal. However, alloy and oxide have different g-factor and linewidth, indicating that paramagnetic ions at different locations play a role in paramagnetic behavior.

3.2. Electrochemical Performance

The CV curves of HEA and HEO at different scan rates are given in **Figure 7**. The CV curves of HEA and HEO exhibit distinct

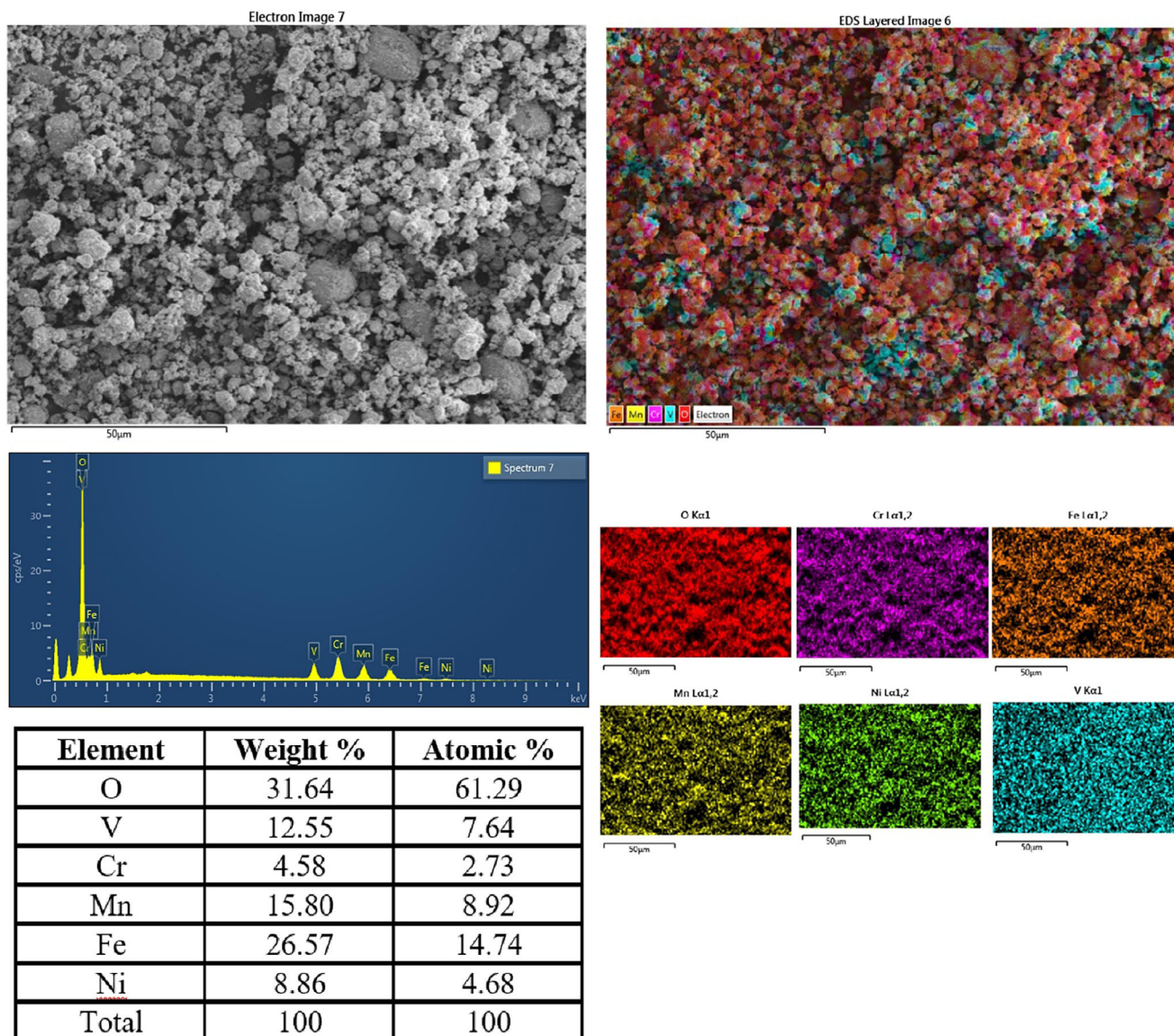


Figure 4. EDX images of the $(\text{Fe}_3\text{Cr}_3\text{Mn}_2\text{NiV})_3\text{O}_4$ -HEO sample.

behaviors, with HEA showing increased current at higher scan rates due to diffusion-controlled processes, while HEO demonstrates surface-controlled redox processes, as indicated by its nearly linear progression at low scan rates.^[22,67] This behavior can be attributed to the structural properties of HEA, as revealed by XRD and SEM analyses, which indicate a combination of amorphous and crystalline phases and a more significant, irregular particle morphology that enhances ion diffusion and charge transfer. The CV curve shape indirectly reflects crystallinity, with sharper redox peaks indicating higher crystallinity and broader peaks suggesting amorphous structures.^[68–70] In this study, the CV curves of HEA and HEO suggest differences in their electrochemical behavior, which align with the XRD results. The XRD analysis confirms a transition from a mixed amorphous-crystalline structure in HEA to a fully crystalline structure in HEO. The CV curves exhibit a nearly linear progression at low

scan rates ($1\text{--}7\text{ mV s}^{-1}$) and then shift to a more distinct curve as the scan rate increases ($20\text{--}200\text{ mV s}^{-1}$). This behavior is compatible with the XRD results, which show that HEO has a fully crystalline structure. As confirmed by XPS analysis, the smaller and spherical particle morphology observed in SEM images enhances the surface area, enabling surface redox reactions and pseudo-capacitive behavior. This outcome implies that the redox processes in the HEO material exhibit reduced kinetics and do not proceed entirely at low scan speeds.^[71] However, the XPS analysis reveals the presence of oxygen vacancies and multiple oxidation states in HEO, which are critical for enhancing pseudo-capacitive behavior and surface redox reactions. The slow kinetics may result from the low ion diffusion rate within the material's structure or the limited number of active sites on the electrode surface, as suggested by the XPS analysis, highlighting the role of oxygen vacancies in facilitating redox reactions.

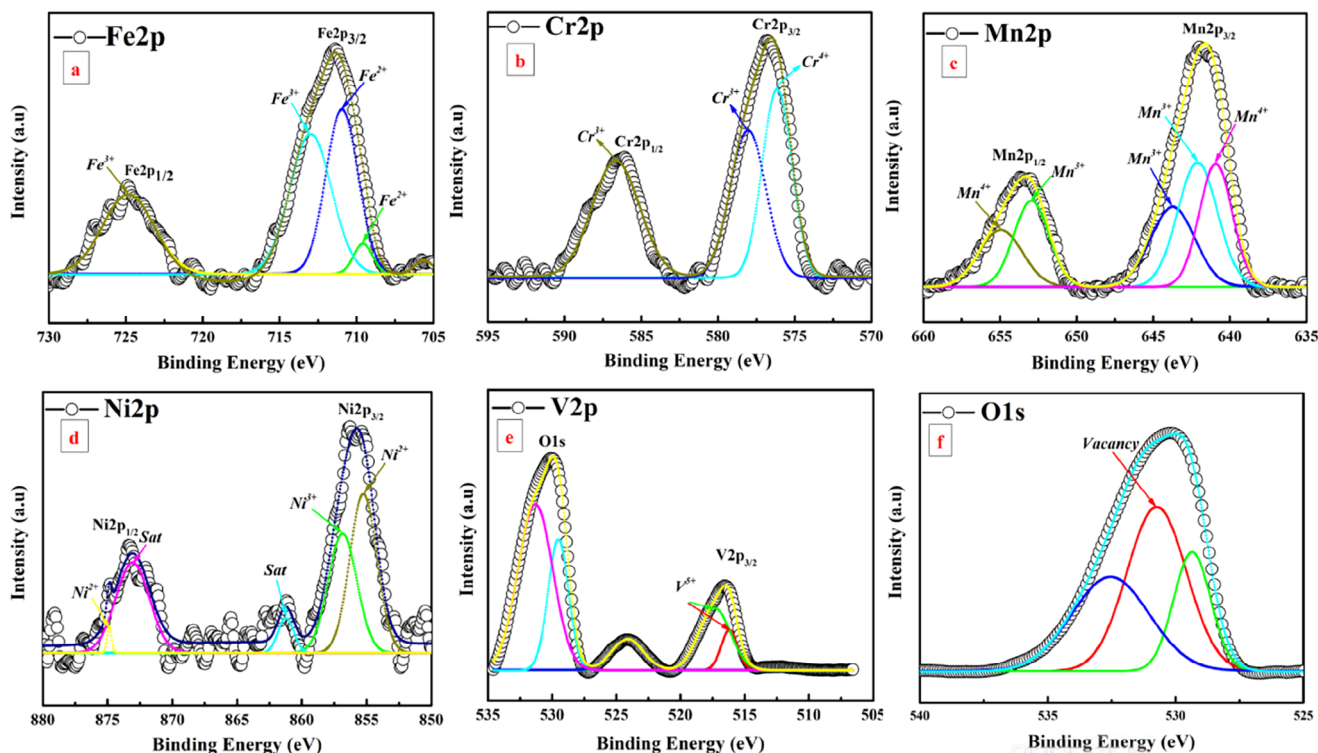


Figure 5. The deconvoluted XPS spectra of Fe 2p, Cr 2p, Mn 2p, Ni 2p, V 2p, and O 1s electrons for the HEO were obtained due to oxidation from the HEA.

The comparison of the CV curves of HEA and HEO electrode materials at a scanning rate of 5 mV s⁻¹ distinctly highlights the variations in the electrochemical behaviors of these materials. The higher current observed in HEA can be linked to their structural regularity and strong magnetic interactions. EPR analysis reveals a sharper resonance signal and lower g-factor indicative of a more isotropic structure and enhanced diffusion-controlled

processes. In contrast, as demonstrated by impedance analysis, the lower charge transfer resistance and enhanced ion conductivity of HEO contribute to their superior surface-controlled processes. This suggests that the HEO material exhibits reduced charge transfer resistance, resulting in a slower reaction rate on the electrode surface. Consequently, it is observed that HEA and HEO electrode materials demonstrate distinct electrochemical behaviors, with HEA favoring diffusion-controlled mechanisms and HEO excelling in surface-controlled redox processes, making them suitable for different energy storage applications. HEA exhibits higher current density and rapid redox kinetics, whereas HEOs are noted for their lower charge transfer resistance and slower redox kinetics. The variations observed will significantly influence the suitability of the materials for various applications.

CV data were examined utilizing the Dunn technique to enhance comprehension of the electrochemical energy storage mechanisms in HEA and HEO electrode materials and the obtained results are given in Figure 8.^[42] This method highlights charge storage techniques by categorizing the CV curves into capacitive and diffusive components at different scan rates. In contrast, the capacitive contribution diminishes as the scan rate is reduced in both HEA and HEO. As the scan rate is reduced, the diffusive contribution increases while the capacitive contribution diminishes in both HEA and HEO. These differences align with the structural and compositional characteristics observed in XRD, SEM, and XPS analyses, where HEA exhibits a mixed amorphous-crystalline structure and larger particle size. At the same time, HEO displays a fully crystalline structure with smaller, spherical particles and oxygen vacancies. The

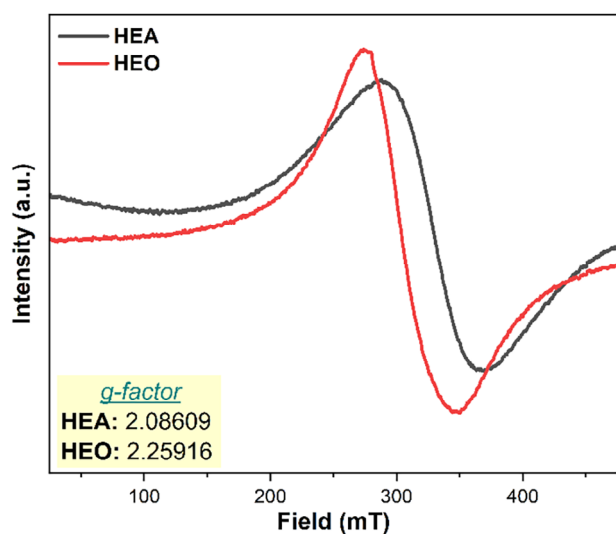


Figure 6. EPR spectra of HEA and HEO sample and their g-factor values.

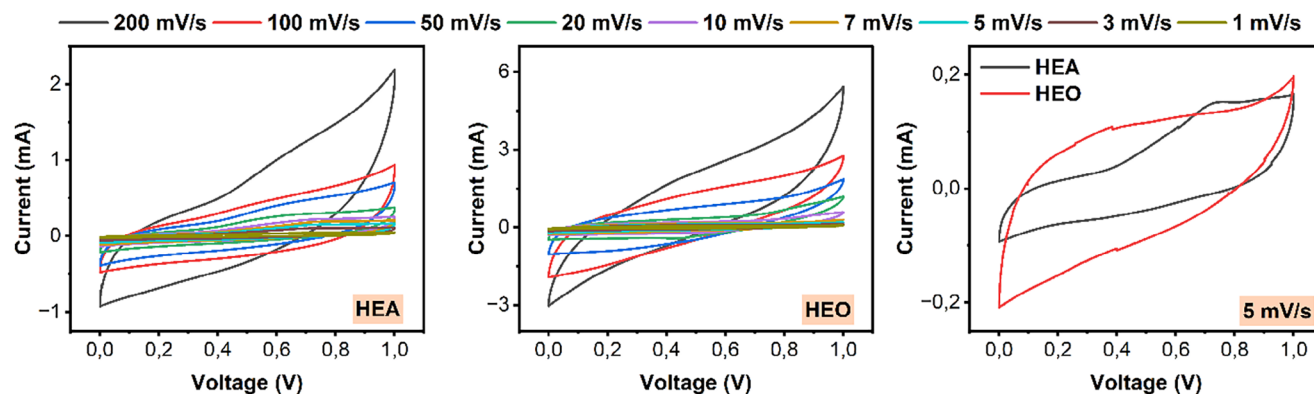


Figure 7. CV curves of HEA and HEO-based designs at different scan rates.

significant diffusive contribution in HEA is supported by their amorphous-crystalline structure and larger particle size. In comparison, the capacitive contribution in HEO is enhanced by their smaller particle size, spherical morphology, and oxygen vacancies. In HEA electrode material, the capacitive contribution declines from 68.1% at a scan rate of 10 mV s^{-1} to 40.3% at 1 mV s^{-1} , whereas the diffusive contribution rises from 31.9% to 59.7%. HEA exhibits a dominant capacitive-controlled mechanism at elevated scan rates, while reduced scan rates allow deeper ion penetration and redox participation. At a scan rate of 5 mV s^{-1} , HEA exhibits a higher diffusive contribution (60.2%), while HEO demonstrates a dominant capacitive contribution (67.1%), con-

sistent with their structural characteristics. These results are compatible with the diffusive and capacitive contributions ratios observed at various scan rates. The distinct impedance behaviors of HEA and HEO directly result from their structural and compositional differences. With their regular structure and strong magnetic interactions, HEA exhibits higher resistance and diffusion-controlled processes. In contrast, the disordered structure and oxygen vacancies in HEO promote surface redox reactions, resulting in lower resistance and enhanced capacitive behavior. The determination of the “b” values for HEA and HEO is illustrated in Figure S3 (Supporting Information), which shows the $\log(i)$ versus $\log(v)$ plots used to calculate these values. The

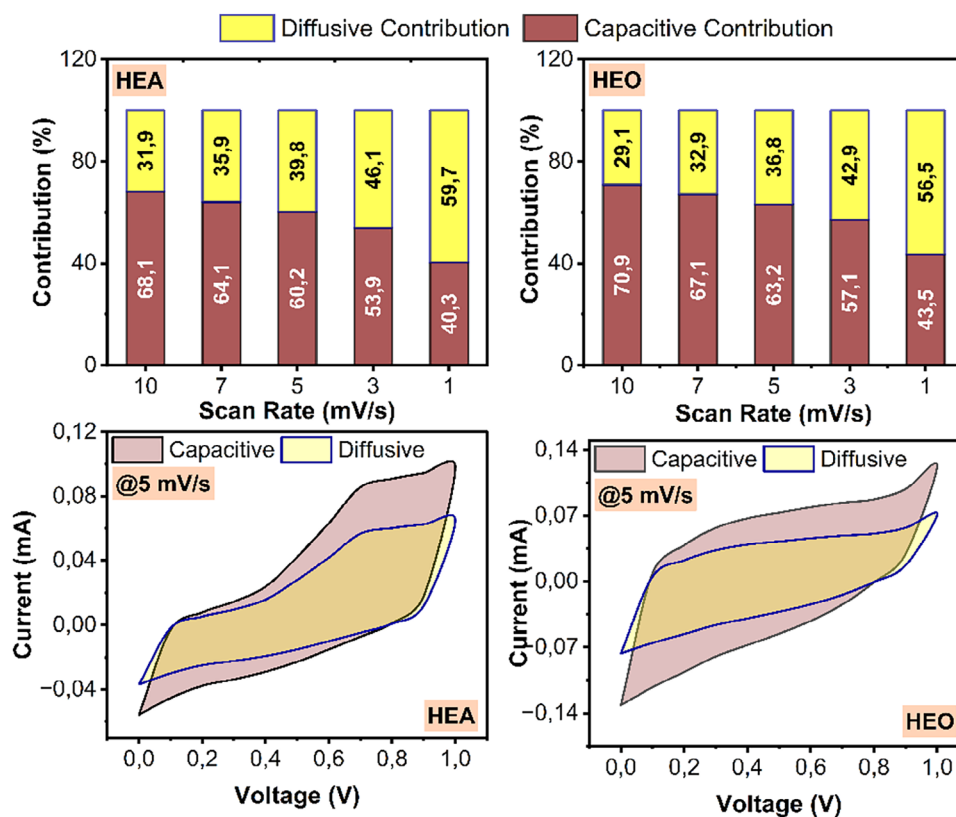


Figure 8. Dunn analysis of HEA and HEO-based supercapacitor designs.

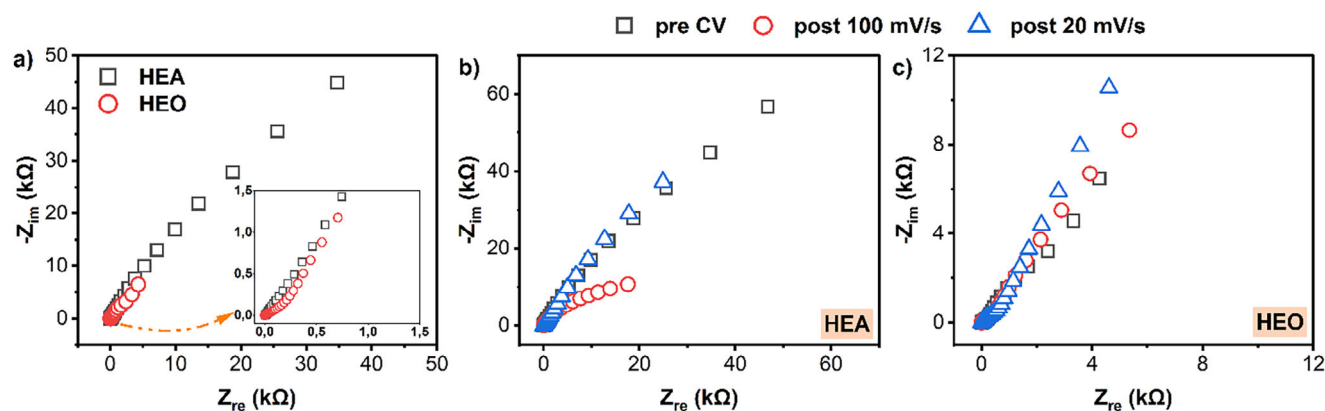


Figure 9. a). Nyquist curves of each synthesized sample, b,c) the Nyquist curves of HEA and HEO before and after CV analysis.

results confirm that HEA exhibits a $b = 0.725$, indicating a significant contribution from diffusion-controlled processes, while HEO demonstrates a $b = 0.757$, highlighting the dominance of surface-controlled pseudo-capacitive mechanisms. The CV analysis highlights that HEA relies on surface and diffusion-controlled processes, while HEO predominantly exhibits surface-controlled redox mechanisms Figure 8.

The results of the impedance analysis offered critical insights into the electrochemical stabilities and kinetic behaviors of HEA and HEO materials.^[72] Figure 9a illustrates that HEA demonstrates high internal resistance (high Z_{re}) in measurements conducted before the CV analysis, while HEO performs with decreased resistance. The higher Z_{re} and R_{ct} values in HEA are due to its mixed amorphous-crystalline structure, while the fully crystalline structure of HEO enhances ion conductivity and surface redox reactions.^[73] As observed in SEM images, the larger and irregular particle morphology of HEA contributes to their higher R_{ct} and diffusion-controlled behavior. Conversely, the smaller and spherical particles of HEO enhance surface area and ion transfer, reducing resistance and improving capacitive behavior. In HEA, a decrease in internal resistance and an improvement in charge transfer resistance (R_{ct}) have been observed in figures taken post-CV, as indicated by the red circle and blue triangle. This situation demonstrates that the active sites on the surface become increasingly accessible during CV analysis, enabling ion transfer. However, the elevated Z_{re} values of HEA suggest that diffusion-controlled processes remain dominant and that kinetic limitations remain. The low Z_{re} and Z_{im} values of HEO show the effectiveness of surface redox reactions and their kinetic benefits. As highlighted by XPS results, the reduced charge transfer resistance (R_{ct}) and enhanced ion conductivity of HEO promote surface redox reactions and pseudo-capacitive mechanisms, which are reflected in the steeper slope of the impedance curve observed after CV analysis. EPR results indicate that HEA's stronger spin-orbit coupling and regular spin alignment support diffusion-controlled processes. In contrast, the broader resonance signal and higher g-factor in HEO reflect structural heterogeneity, enhancing surface redox reactions and capacitive behavior. The lower resistance values and steeper slope in the Nyquist curve of HEO align with the increased current density and distinct redox peaks observed in CV analysis. Similarly, the higher R_{ct} and Z_{re} values of HEA are consistent with their lower current density and

the dominance of diffusion-controlled processes, as indicated by CV analysis.

Detailed examination of the Nyquist curves revealed a broader semicircle in the Nyquist curve for HEA, signifying an increased charge transfer resistance (R_{ct}) for the material. The smaller semicircle of HEO suggests that surface redox reactions are more efficient, and that charge transfer occurs with a higher probability.^[74] HEO's starting point (Z_{re}) is lower than HEA's, implying that HEO exhibits lower electrolyte resistance (R_s). The steeper slope of HEA in the low-frequency region indicates an elevated dominance of diffusion-controlled processes in this material.^[74] Figure S1 and Table S2 (Supporting Information) present experimental and modeling results showing that the two materials exhibit distinct kinetic and diffusion properties. The equivalent circuit model for HEA demonstrates that diffusion-controlled processes prevail, as evidenced by a significant charge transfer resistance ($R_2 = 1659.2 \, \Omega$) and a Warburg element ($W_3 = 1122.2 \, \Omega \, s^{-1/2}$), indicating more significant kinetic limitations. The equivalent circuit model of HEO reveals a higher degree of capacitive behavior, characterized by a lower charge transfer resistance ($R_2 = 36.4 \, \Omega$) and reduced diffusion effect ($W_4 = 4915.3 \, \Omega \, s^{-1/2}$). In contrast, the reduced Warburg element ($W_4 = 4915.3 \, \Omega \, s^{-1/2}$) in HEO reflects enhanced ion transfer and capacitive behavior.^[75] The reduced electrolyte resistance ($R_1 = 11.5 \, \Omega$) and elevated capacitance values ($C_1 = 1.53 \times 10^{-6} \, F$, $C_3 = 251.2 \times 10^{-6} \, F$) of HEO enhance the efficiency of surface redox reactions and facilitate ion transfer.^[76] Evaluation of these results through CV and GCPL analyses reveals that HEO displays distinct redox peaks and increased current density, attributed to reduced charge transfer resistance and enhanced conductivity. HEA's elevated charge transfer resistance and reliance on diffusion-controlled processes correlate with the reduced current density observed in the CV analysis and the abbreviated discharge time noted in the GCPL analysis. Moreover, the significant Warburg component of HEA suggests that this material exhibits greater kinetic limitations and facilitates ion transfer more readily.

Figure 10a presents the specific capacity (mAh/g) values obtained from GCPL analysis, which reflects the charge storage capability of the materials. This is distinct from specific capacitance (F/g). The specific capacity (mAh/g) values in Figure 10a reveal that HEO exhibits a significantly higher capacity than HEA. This observation aligns with the $b = 0.757$ value obtained from Dunn

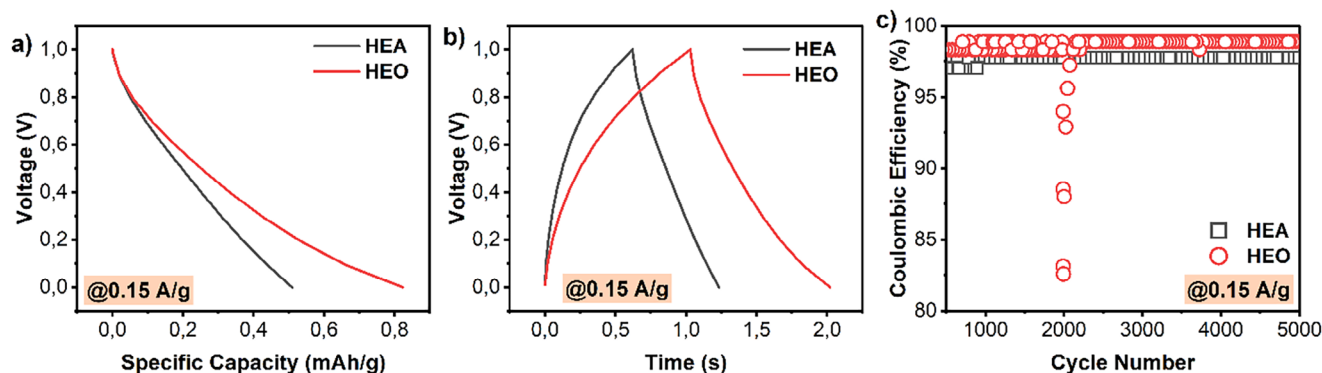


Figure 10. a) specific capacity of HEA and HEO designs, b) charge/discharge time of HEA and HEO, and c) coulombic efficiency of HEA and HEO designs at 0.15 A g⁻¹.

analysis, indicating that surface-controlled capacitive processes predominantly govern HEO. The superior energy storage mechanisms of HEO, driven by surface redox reactions, are further supported by the distinct redox peaks observed in the CV analysis. In contrast, the reduced capacity of HEA correlates with the $b = 0.725$ value, suggesting a more substantial contribution from diffusion-controlled processes. Furthermore, Figure S3 (Supporting Information) illustrates the variation in specific capacity for HEA and HEO at the end of the initial five and final five cycles. HEO demonstrates superior cycling stability, with minimal changes in specific capacity, attributed to its surface-controlled redox reactions and pseudo-capacitive behavior. In contrast, HEA exhibits a more significant decline in specific capacity, reflecting the limitations of its diffusion-controlled processes and structural degradation over extended cycling. Figure 10b compares the charge and discharge profiles of the materials, highlighting the extended discharge time of HEO, which reflects their greater energy storage capacity. Conversely, the shorter discharge time of HEA indicates the influence of diffusion-controlled processes, which limit ion mobility and energy storage efficiency. As revealed by impedance analysis, the reduced internal resistance and more stable voltage profile of HEO further emphasize their kinetic advantages and the effectiveness of surface redox reactions. Coulombic efficiency (CE, %) was evaluated over 5000 cycles. The greater stability in Coulomb efficiency of HEO, as shown in Figure 10c, is attributed to its fully crystalline structure and the presence of oxygen vacancies, which enhance surface redox reactions and minimize degradation during cycling. In contrast, the mixed amorphous-crystalline structure of HEA and its reliance on diffusion-controlled processes result in higher internal resistance and fluctuations in Coulomb efficiency over time. These differences highlight the superior cycling stability of HEO, making it a more reliable candidate for long-term energy storage applications. Both materials demonstrated high coulombic activity; however, HEO exhibited superior cycling stability, maintaining a coulombic efficiency exceeding 95% throughout the 5000 cycles. In contrast, HEA displayed more significant fluctuations in efficiency over time, indicating less stable energy storage mechanisms. These results suggest that HEO possess more reliable and stable energy storage mechanisms, primarily reliant on surface redox reactions, enabling them to sustain performance over extended cycles. Additionally, the drop in coulombic effi-

ciency of HEO at 2000 cycles, as shown in Figure 10c, is attributed to the gradual degradation of the electrode material during prolonged cycling. This includes structural changes such as the partial dissolution of transition metal ions, the formation of passivation layers, or the accumulation of reaction by-products, which can hinder ion transport and reduce charge transfer efficiency. Despite this temporary drop, the coulombic efficiency stabilizes above 95% for the remaining cycles, demonstrating the overall stability and reliability of the HEO electrode. The GCPL analysis results, consistent with findings from CV and Dunn analyses, confirm that HEO exhibits a greater tendency toward surface-controlled processes, resulting in enhanced capacity and cycling stability. These characteristics, combined with their reduced internal resistance and efficient ion transfer, make HEO a more suitable candidate for high-performance supercapacitor applications than HEA.

3.2.1. Effect of Transition Between HEA and HEO on Supercapacitor Electrode Performance

This study investigates the effects of the transformation between HEA and HEO on the performance of supercapacitor electrodes. The electrochemical performance parameters in Table 6 demonstrate the fundamental differences in the energy storage mechanisms of HEA and HEO. The specific capacitance of HEO is 294.0 F g⁻¹, which is more than double that of HEA at 141.4 F g⁻¹. This difference is related to the tendency of HEO to promote surface redox reactions and exhibit pseudo-capacitive behavior. CV and Dunn analyses suggest that HEO provides 67.1% of capacitance, whereas HEA provides only 40.3%. The irregular structure of HEO, along with its smaller and spherical particle morphology (as confirmed by SEM results) and the presence of oxygen vacancies (as shown by XPS results),

Table 6. Electrochemical parameters of HEA and HEO design.

Design	Specific Capacitance, [F g ⁻¹]	Energy Density, [Wh kg ⁻¹]	Power Density, [Wh kg ⁻¹]
HEA	141.4	19.6	11.4
HEO	294.0	40.8	14.3

enhances the number of active sites, enabling surface redox reactions, leading to high capacitance. The energy density of HEO is 40.8 Wh kg^{-1} , which is significantly higher than that of HEA at 19.6 Wh kg^{-1} . GCPL analyses confirm the high energy storage capacity and expanded discharge period of HEO. This shows the efficacy of the energy storage mechanism of HEO, which is predicated on surface-controlled processes. The decreased discharge time of HEA means that diffusion-controlled processes dominate, and ion mobility is limited. The power density of HEO is 14.3 kW kg^{-1} , exceeding that of HEA at 11.4 kW kg^{-1} . The observed difference is due to the lower internal resistance ($R_1 = 11.5 \Omega$) and charge transfer resistance ($R_2 = 36.4 \Omega$) values of HEO. Impedance analyses reveal that the ion conductivity of HEO is higher and that surface redox reactions proceed at faster speeds. The increased charge transfer resistance ($R_2 = 1659.2 \Omega$) and internal resistance ($R_1 = 7.8 \Omega$) values of HEA point to diffusion-controlled processes dominate, which suggests the presence of kinetic limitations. EPR analyses indicate that the ordered structure of HEA is defined by a lower g-factor (2.08609) and a more distinct resonance signal. This suggests that HEA shows strong magnetic interactions and a more ordered spin structure, making it vulnerable to diffusion-controlled processes. The higher g-factor (2.25916) and the broader resonance signal of HEO reveal its disordered structure and tendency to surface redox reactions. The structural differences enhance the pseudo-capacitive behavior of HEO. This transformation between HEA and HEO presents significant benefits for their application as electrode materials in supercapacitors. The capacitive behavior of HEO due to surface redox reactions leads to increased energy and power density, whereas the susceptibility of HEA to diffusion-controlled processes results in decreased efficiency.

4. Conclusion

This study thoroughly examined the behavior of HEA and HEO as materials for the electrodes of supercapacitors. Characterization studies revealed that HEA has an ordered structure, making them prone to diffusion-controlled processes. In contrast, HEO demonstrates capacitive behavior due to their disordered structure and propensity for surface redox reactions. Electrochemical analyses indicated that HEO exhibited superior specific capacitance (294.0 F g^{-1}), energy density (40.8 Wh kg^{-1}), and power density (14.3 kW kg^{-1}) compared to HEA. The Dunn analysis further confirmed that HEO predominantly relies on capacitive processes, while diffusion-controlled mechanisms mainly drive HEA. Impedance analyses revealed that HEO exhibits reduced internal resistance and enhanced ion conductivity, whereas HEA is characterized by higher resistance and kinetic limitations. EPR analyses provided critical insights into the structural and magnetic differences between HEA and HEO. The ordered structure of HEA, characterized by a lower g-factor and sharper resonance signal, promotes strong magnetic interactions and diffusion-controlled processes. In contrast, the disordered structure of HEO, with a higher g-factor and broader resonance signal, supports surface redox reactions and pseudo-capacitive behavior. These findings highlight the significant impact of structural and magnetic differences on the electrochemical performance of these materials.

Unlike most studies that utilize three-electrode systems, this work employed a two-electrode system, providing real-world application insights and addressing a critical gap in the field. The results demonstrate that HEA and HEO exhibit distinct energy storage mechanisms, suggesting that these materials can be optimized for supercapacitor applications. With its superior performance derived from surface redox reactions, HEO is suitable for applications requiring high energy and power density. At the same time, HEA may be ideal for applications where diffusion-controlled processes are advantageous.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Data Availability Statement

Research data are not shared.

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