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A Novel Spinel High-Entropy Oxide ($\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}$) $_3\text{O}_4$ as Anode Material for Lithium-Ion Batteries

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Abstract: In this study, we synthesized spinel high-entropy oxide (HEO) ($\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}$) $_3\text{O}_4$ nanoparticles by a simple solution combustion method. These particles were investigated for their performance as anodes in lithium-ion batteries. The reversible capacity is 132 $\text{mAh}\cdot\text{g}^{-1}$ after 100 cycles at a current density of 100 $\text{mA}\cdot\text{g}^{-1}$, 107 $\text{mAh}\cdot\text{g}^{-1}$ after 1000 cycles at a current density of 1 $\text{A}\cdot\text{g}^{-1}$, and 96 $\text{mAh}\cdot\text{g}^{-1}$ rate capacity at a high current density of 2 $\text{A}\cdot\text{g}^{-1}$. The outstanding cycle stability under high current densities and remarkable rate performance can be attributed to the stable structure originating from the high entropy of the material.

Keywords: high-entropy oxide; lithium-ion battery; spinel; nanoparticle; anode



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1. Introduction

Lithium-ion batteries (LIBs) have seen swift adoption in consumer electronics and electric vehicles [1–5]. However, existing research has yet to satisfy the growing demand for batteries with higher electrochemical lithium storage performance. A key limitation lies in the lithium storage capabilities of anode materials [6,7]. Currently, the widely used commercial anode materials for LIBs—natural or synthetic graphite—have a specific capacity of only 372 $\text{mAh}\cdot\text{g}^{-1}$, which can no longer meet the demands for high energy density and high-rate performance in the next generation of lithium-ion batteries. Commonly studied anode materials, including transition metal oxides [8,9] and silicon [10], undergo significant volume expansion during lithium intercalation/deintercalation. This expansion can lead to electrode structural failure and increased internal resistance, which in turn degrade lithium storage performance. Hence, the innovation of novel anode materials is essential.

A material that has shown promise in anode materials is the high-entropy oxide (HEO). Derived from the concept of high-entropy alloys (HEAs) [11–14], HEOs are composed of five or more metals in equal molar amounts, leading to notable alterations in composition, structure, and properties. HEOs leverage configurational entropy for phase stabilization [15], with higher entropy generally correlating with greater phase stability. Unlike other materials like transition metal oxides (TMOs), which depend on intrinsic energy for phase stabilization and have crystal structures determined by energy minimization under specific conditions, HEOs with five or more metal elements demonstrate potential for innovative lithium storage performance.

In 2016, Berardan [16] first introduced HEOs, emphasizing the unique properties stemming from their elevated configurational entropy. In 2018, Sarkar [17] et al. synthesized a rock salt structured HEO, ($\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}$)O, via pyrolysis, which showed a specific capacity of 770 mAh/g after 100 cycles at 200 mA/g . That year, Qiu [18] et al. created

(MgCoNiCuZn)O HEOs by a solid-phase reaction, showcasing an initial discharge capacity of 1585 mAh/g and excellent cycling stability; after 300 cycles at 100 mA/g, it retained a reversible capacity of 920 mAh/g. Even at 3000 mA/g, it maintained 490 mAh/g. In 2020, Wang [19] et al. developed a spinel-structured HEO, $(\text{FeCoNiCrMn})_3\text{O}_4$, with outstanding cycling stability and rate performance due to its large lattice parameter facilitating 3D ion and electron diffusion. The anode, composed of five elements with diverse valences, induced lattice distortions and electronic modifications, enhancing conductivity and lithium storage. In 2021, Chen [20] et al. detailed the lithium storage mechanism of the spinel HEO $(\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Ti}_{0.2})_3\text{O}_4$, which delivered a high capacity of 560 mAh/g at 100 mA/g. Duan [21] et al. synthesized single-phase spinel HEOs, $(\text{FeCoNiCrMnXLi})_3\text{O}_4$ ($X = \text{Cu, Mg, Zn}$), with seven metal elements in equal molar ratios, enhancing LIB anode performance through rapid 3D Li^+ transport and entropy-driven stabilization. Rock salt-structured HEOs exhibit durable and reversible lithium storage due to the entropic stabilization effect, enhancing their cyclic stability [22,23]. In contrast, spinel-structured HEOs, which include metal cations with a broader range of oxidation states from divalent to tetravalent [24], can cause larger lattice distortions and more defects, and greatly alter the electronic structure. These effects improve electrical conductivity, ion diffusion, and lithium storage capacity [25–27]. However, despite these advantages for lithium-ion batteries, the utilization of HEOs in these applications remains limited.

Researchers in this field are predominantly engaged in material exploration and the enhancement of their electrochemical lithium storage properties. However, a universal framework for material design has not yet been established. The element selection for HEO synthesis poses a critical challenge in leveraging HEOs as anode materials in lithium-ion batteries (LIBs). There is an urgent need for a coherent strategy to design HEOs with diverse structures and high specific capacities. For instance, our strategy for spinel-structured HEOs encompasses three key aspects: (1) structural stability, ensuring that the ionic radii of the ions in the HEO, normalized by their coordination numbers, are nearly the same; (2) ionic valence selection that satisfies the chemical formula, where variable valences of ions in the HEO must align with the formula's requirements; for a spinel with AB_2O_4 , suitable valences might be A^{2+} and B^{3+} or A^{4+} and B^{2+} ; and (3) achieving a high specific capacity by formulating the HEO to allow for the reduction of high-valence metal cations to elemental metals or lithium alloys during lithiation, requiring the constituent simple oxides to possess a high theoretical specific capacity. By adhering to these principles, a variety of HEOs can be engineered with properties optimized for superior performance in energy storage, catalysis, and sensing applications. On this basis, we have successfully developed a novel HEO, $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$, tailored for electrochemical lithium storage.

2. Results

The XRD pattern in Figure 1a confirms the successful synthesis of $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$ with a single-phase spinel structure (space group Fd-3m). As illustrated in Figure 1, the diffraction peaks at 2θ of 18.71° , 30.78° , 36.27° , 37.94° , 44.10° , 54.74° , 58.37° , 64.13° , and 75.95° correspond to (111), (220), (311), (222), (400), (422), (511), (440), and (533) crystal planes of $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$, respectively. No impurity phase was observed, indicating that $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$ forms a single-phase spinel structure. The Rietveld method (software: FullProf(64 bits), Version: 5-May-2020) was performed based on the XRD data using the space group of Fd3m. Figure 1b shows the fitting results; the lattice constant, density, and crystallite size of the sample are determined to be 8.289 Å, 9.250 g/cm³, and 28.0 nm, respectively.

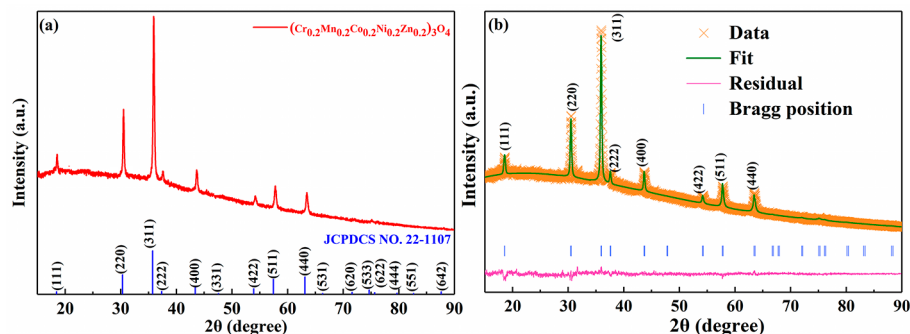


Figure 1. (a) XRD pattern; (b) Rietveld refinement pattern of the $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$ nanoparticles.

Figure 2 displays the morphology and microstructure of the $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$ nanoparticles. The SEM image (a) and TEM image (g) represent the overall particle structure at low and high magnification, respectively. As seen in the detailed illustration in Figure 2g, the nanoparticles exhibit a relatively narrow distribution range of particle diameter (10.9–67.7 nm), with an average particle diameter of approximately 28 nm. This is attributed to the short calcination time (40 min) and the influence of high-temperature gas during calcination, which prevents further growth and aggregation of nanoparticles. EDS mapping confirms the presence of massive metallic elements Cr (Figure 2b), Mn (Figure 2c), Co (Figure 2d), Ni (Figure 2e), and Zn (Figure 2f) within the $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$ nanoparticles, with similar distribution densities observed. Quantitative analysis of each element's content was performed, and the results are presented in Table 1. The atomic proportions of Cr, Mn, Co, Ni, and Zn elements are approximately equal, aligning with our experimental goals. The high-resolution TEM image in the inset of Figure 2g indicates that the well-resolved interplanar spacing of the lattice fringe is about 0.285 nm, which corresponds to the (220) plane of spinel-structured $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$.

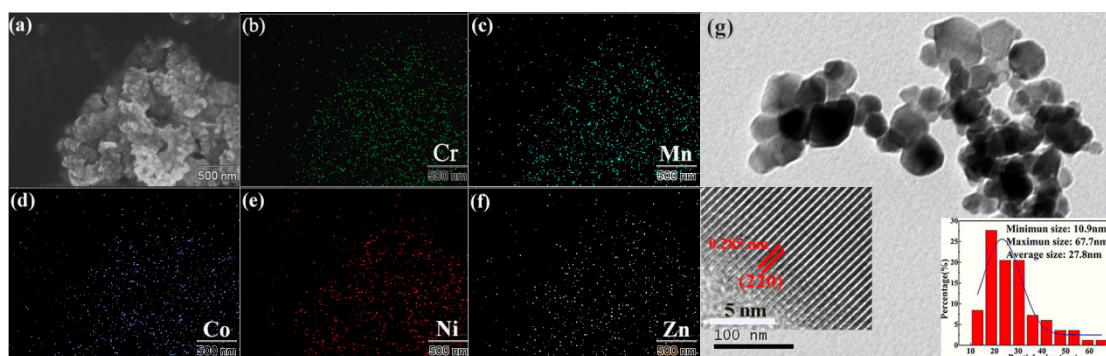


Figure 2. SEM image (a) and corresponding EDS elemental maps of Cr (b), Mn (c), Co (d), Ni (e), and Zn (f), and TEM image (g) of $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$ nanoparticles. The inset in (g) shows the distribution of the particle size.

Table 1. The atomic fraction of each element in the HEO sample.

Element	Atomic Fraction (%)
O	63.65
Cr	7.69
Mn	7.60
Co	7.08
Ni	7.29
Zn	6.69

Figure 3 illustrates the electrochemical lithium storage performance. Figure 3a illustrates the initial three cyclic voltammetry (CV) cycles tested at a scan rate of 0.1 mV/s. The initial cathodic scan of the cell exhibits an initial reduction peak around 0.965 V, which can be attributed to the reduction of metal cations in the HEO to metals, along with the formation of Li_2O [16]. Subsequently, a significant irreversible reduction peak emerges between 0 and 0.5 V due to the formation of the SEI film [17]. The disappearance of this irreversible peak in subsequent scans suggests that the quantity of SEI film generated remains essentially stable. In the first anodic scan, oxidation peaks are observed over a broad range of 1.0–2.0 V [28,29], with similar peaks in this range observed in subsequent scans, indicating a continuous and reversible oxidation process. The reactions that occur during this redox process are shown in Equation (1):

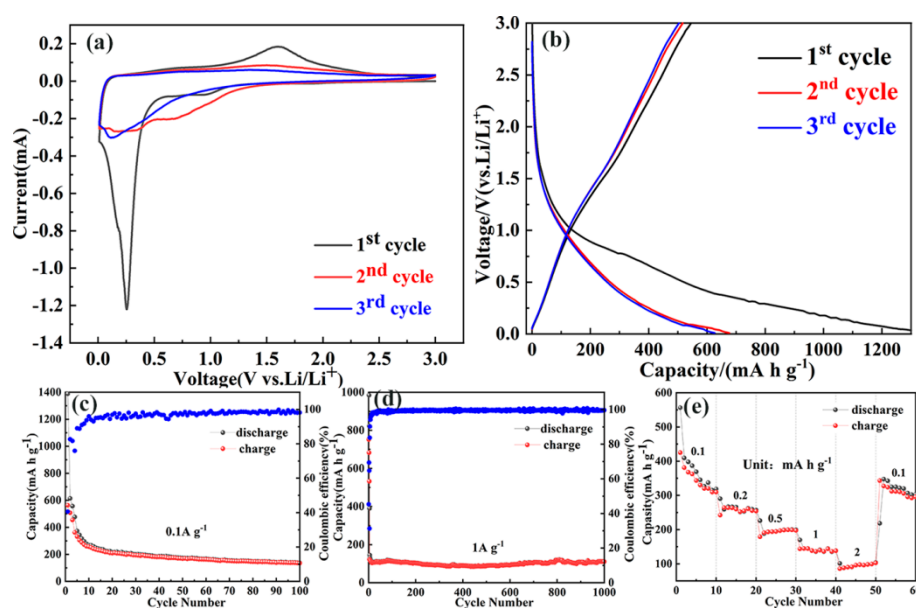
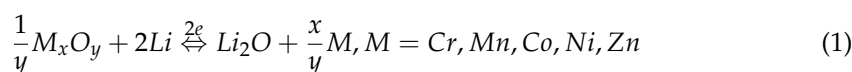


Figure 3. CV curves at a scan rate of 0.1 $\text{mV}\cdot\text{s}^{-1}$ (a), discharge/charge profiles at 100 $\text{mA}\cdot\text{g}^{-1}$ (b), cycling performance at 100 $\text{mA}\cdot\text{g}^{-1}$ (c), long-term cycling performance at 1 $\text{A}\cdot\text{g}^{-1}$ (d), and rate capability of $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$ electrode (e).

Figure 3b presents the discharge/charge profiles at a current density of 100 $\text{mA}\cdot\text{g}^{-1}$. Initially, a small discharge plateau around 0.965 V signifies the lithiation process of HEO. Subsequently, the discharge curve shows a gradual voltage drop until reaching the lower cutoff limit of 0.01 V, indicating the formation of SEI films due to the electrolyte decomposition and the interfacial lithium storage interaction [16]. During the charge process, the curve exhibits a continuously increasing potential slope up to approximately 1.6 V, attributed to the reversible oxidation of active metals to oxides. From Figure 3b, it can be seen that the first-turn charge-specific capacity/discharge-specific capacity of the HEO is 563/1388 $\text{mAh}\cdot\text{g}^{-1}$, and the first-time coulombic efficiency of the HEO electrode is low, only 40.6%.

Figure 3c,d represent the cycling performance at 100 $\text{mA}\cdot\text{g}^{-1}$ and 1 $\text{A}\cdot\text{g}^{-1}$, respectively. As shown in Figure 3c, the specific capacities initially decay rapidly during the first 10 cycles, followed by a slower degradation during the subsequent cycles until reaching a stable capacity of 132 $\text{mAh}\cdot\text{g}^{-1}$. The low initial Coulombic efficiency (40.6%) is inherent to transformed anodes, primarily caused by the formation of the SEI film [30]. During subsequent cycles, particularly the second and third cycles, the charging and discharging processes induce some collapse and fragmentation of the active material, resulting in the

formation of additional SEI membrane and a consequent capacity decrease. By the tenth cycle, the active material stabilizes, preventing further structural degradation and SEI formation, thus stopping rapid capacity loss. However, ongoing volume fluctuations can still cause some active material to detach from the current collector, leading to a gradual attenuation of capacity in subsequent cycles, albeit at a slow rate. Figure 3d demonstrates the stable cycling performance at 1 A g^{-1} with the specific capacity reaching 107 mAh g^{-1} after 1000 cycles.

Figure 3e presents the rate capability at different current densities. It is evident that the specific capacity decreases rapidly at a low current density but exhibits no decay at higher current densities due to the side reaction during the lithiation/delithiation processes [16,17,31]. At low current densities, the battery charging and discharging time is longer, which allows more time for side reactions to occur in the electrolyte. This could lead to the loss of active lithium and the thickening of the SEI layer, thereby accelerating capacity decay. The discharge/charge curves show a high degree of overlap during different current densities. When the current density abruptly switched back to 0.1 A g^{-1} from 2 A g^{-1} , the specific capacity recovered to 319 mAh g^{-1} with a capacity retention rate of 97.8%, indicating that the entropy stability effect contributes to the stability of the LIB anode. Table 2 lists the electrochemical experimental results of the spinel-structured HEO in this study compared with those of other spinel-structured HEOs when used as LIB anode materials, which demonstrates that the novel spinel-structured HEO, as synthesized in this study, exhibits potential for lithium storage capabilities in lithium-ion batteries.

Table 2. Synthesis methods and electrochemical properties of spinel-type HEOs.

Materials	Method	Rate Capability/ mAh g^{-1}	Cyclic Performance (Cycles)/ mAh g^{-1}	Ref.
$(\text{MgFeCoNiZn})_3\text{O}_4$	Solid-state synthesis	$304 @ 0.5 \text{ A g}^{-1}$	$360(300) @ 0.1 \text{ A g}^{-1}$	[32]
$(\text{MgTiZnNiFe})_3\text{O}_4$	Solid-state reaction	$93.6 @ 1 \text{ A g}^{-1}$	$145(100) @ 0.1 \text{ A g}^{-1}$; $100(800) @ 1 \text{ A g}^{-1}$	[33]
$(\text{CoTiZnNiFe})_3\text{O}_4$	Solid-state reaction	$150.3 @ 1 \text{ A g}^{-1}$	$290(100) @ 0.1 \text{ A g}^{-1}$; $130(800) @ 1 \text{ A g}^{-1}$	[33]
$(\text{FeNiCrMnMgAl})_3\text{O}_4$	Solution combustion	$350 @ 4 \text{ A g}^{-1}$	$670(200) @ 0.2 \text{ A g}^{-1}$	[34]
$(\text{MnFeCoNiZn})_3\text{O}_4$	Electrospinning	$58 @ 2 \text{ A g}^{-1}$	$155(550) @ 0.5 \text{ A g}^{-1}$	[35]
$(\text{CrFeMnNiCo}_2)_3\text{O}_4$	Sol-gel	$147 @ 2 \text{ A g}^{-1}$	$520(100) @ 0.2 \text{ A g}^{-1}$; $120(1000) @ 2 \text{ A g}^{-1}$	[36]
$(\text{CrFeMnNiCo}_3)_3\text{O}_4$	Sol-gel	$101 @ 2 \text{ A g}^{-1}$	$505(100) @ 0.2 \text{ A g}^{-1}$; $118(1000) @ 2 \text{ A g}^{-1}$	[36]
$(\text{CrFeMnNiCo}_4)_3\text{O}_4$	Sol-gel	$97.2 @ 2 \text{ A g}^{-1}$	$510(100) @ 0.2 \text{ A g}^{-1}$; $105(1000) @ 2 \text{ A g}^{-1}$	[36]
$(\text{CrMnCoNiZn})_3\text{O}_4$	Sol-gel	$96 @ 2 \text{ A g}^{-1}$	$132(100) @ 0.1 \text{ A g}^{-1}$; $107(1000) @ 1 \text{ A g}^{-1}$	This work

We also explored the dynamic properties of the HEO electrode using electrochemical impedance spectroscopy (EIS). Initial impedance measurements were performed before cycling (HEO-0) and after 20 cycles at a current density of 0.1 A g^{-1} (HEO-20), as shown in Figure 4. The Nyquist plots featured semicircles at mid-to-high frequencies and linear trends at low frequencies. For analyzing the impedance data, we applied an equivalent circuit model that included the solution resistance (R_s), charge transfer resistance (R_{ct}), a constant phase element (CPE) representing the mid-frequency semicircle, and Warburg impedance (W) for Li^+ diffusion representing the linear features at low frequencies. The R_{ct} values, obtained from impedance fitting, are 282Ω for HEO-20 and 389Ω for HEO-0, respectively. It is evident that R_{ct} of the HEO after 20 cycles is lower than that of the HEO before cycling.

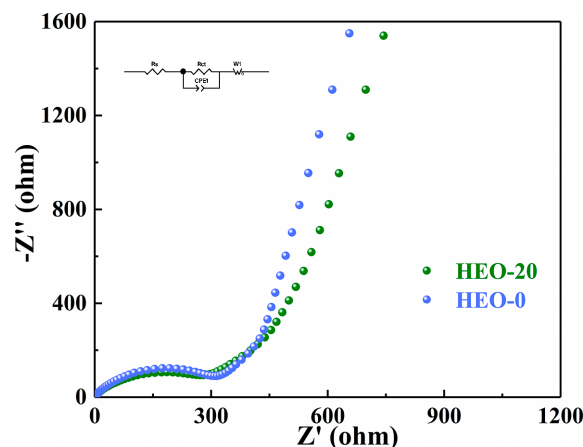


Figure 4. EIS plots of HEO electrode before (HEO-0) and after 20 cycles (HEO-20) at 0.1 A g^{-1} .

X-ray photoelectron spectroscopy (XPS) was employed to examine the elemental composition and chemical valence state changes of HEO before and after 1000 cycles at 1 A g^{-1} , which confirmed the presence of Cr, Mn, Co, Ni, Zn, and O and the corresponding valence states before and after cycling (as depicted in Figure S1). Figure 5 shows the Co 2p and Ni 2p spin–orbit peaks before and after 1000 cycles, which identify the oxidation states of the elements. The Co 2p spectrum in Figure 5a, fitted with Gaussian shapes before cycling, displays four main peaks at 779.3, 781.2, 794.6, and 796.5 eV, along with two satellite peaks at 787.9 and 803.4 eV. The peaks at 779.3 and 794.6 eV are attributed to Co^{3+} , while the peaks at 781.2 and 796.5 eV correspond to the $2p_{3/2}$ and $2p_{1/2}$ transitions of Co^{2+} , respectively. The approximately 15.5 eV energy difference between the Co $2p_{3/2}$ (781.2/779.3 eV) and Co $2p_{1/2}$ (796.5/794.6 eV) peaks is characteristic of cobalt in both +2 and +3 oxidation states. The Ni 2p XPS spectrum in Figure 5c, also fitted with Gaussian shapes before cycling, shows four principal peaks at 853.5, 855.5, 871.5, and 873.2 eV, accompanied by two satellite peaks at 860.6 and 878.3 eV. The binding energies at 853.5/855.5 eV and 871.5/873.2 eV are indicative of Ni^{2+} and Ni^{3+} , respectively. Figure 5b,d illustrate the chemical valence states of Co and Ni after cycling. After 1000 cycles, the presence of Co^{3+} and Ni^{3+} ions is minimal, with a decrease in divalent ion content, replaced by amounts of metals Co and Ni. This could be due to the irreversible reactions of Co^{3+} and Ni^{3+} during the lithium intercalation/delithiation process, leading to the formation and residue of metals Co or Ni during cycling.

Figure 6a,b present SEM images of the HEO electrodes before and after 1000 cycles at a current density of 1 A g^{-1} . After cycling, the initial nanoparticles coalesced into larger clusters, with the appearance of microcracks and voids, which are tens of nanometers in size. This indicates that volume changes are linked to the charge and discharge processes. Although microcracks form due to particle aggregation, the elimination of inter-particle gaps leads to denser packing of the aggregates, which improves electrical conductivity. This conjecture is consistent with the results obtained from the EIS measurements. The corresponding EDS images in Figure 6c–h show a uniform distribution of Cr, Mn, Co, Ni, and Zn across the electrode surface. This uniformity suggests that the HEO maintains its structural integrity after 1000 cycles, consistent with the observed stability of long cycle performance under high current.

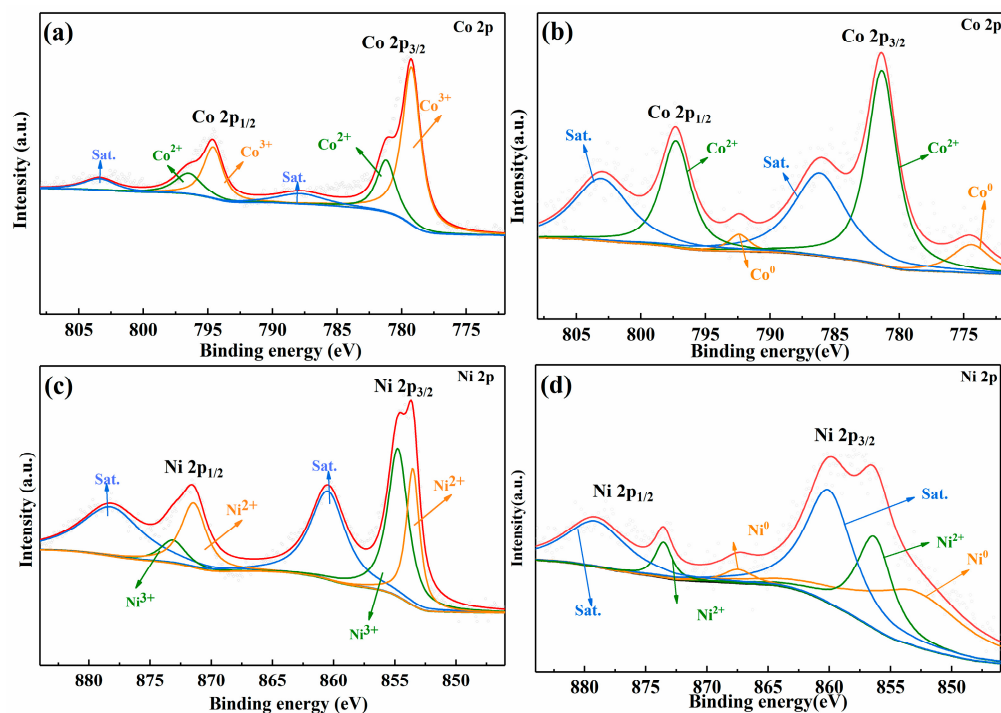


Figure 5. XPS spectra of Co 2p (a) and Ni 2p (c) of HEO before cycling and XPS spectra of Co 2p (b) and Ni 2p (d) of HEO after 1000 cycles at 1 A g^{-1} .

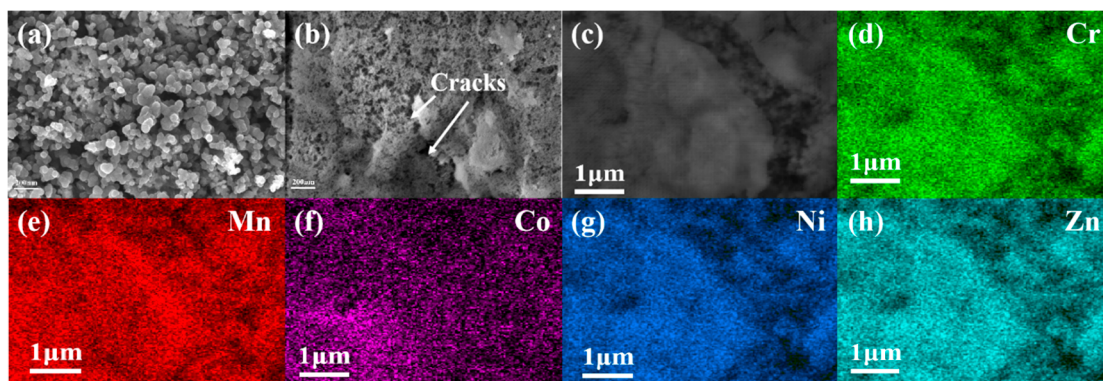


Figure 6. SEM image of HEO before (a) and after (b) 1000 cycles at a current density of 1 A g^{-1} ; corresponding elemental mapping of all elements (c), and corresponding elemental mapping of Cr (d), Mn (e), Co (f), Ni (g), and Zn (h) of the HEO.

3. Conclusions

We synthesized a novel spinel-structured HEO ($\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}_4$) and thoroughly investigated its electrochemical lithium storage performance as an anode material for LIBs. This anode material demonstrates good rate capability and long-term cycling stability at elevated current densities, attributed to the entropy stabilization effect characteristic of high-entropy oxides (HEOs). However, the material's low initial Coulombic efficiency of 40.6% and the observed capacity degradation after 10 cycles at low current densities pose challenges for its development as an anode material for LIBs. To address these electrochemical issues, strategies such as material composite formation or the fabrication of artificial SEI could be employed to enhance electrochemical performance. The artificial SEI on the surface of HEO can reduce the amount of lithium ions required for SEI formation, while also decreasing the consumption of lithium ions by surface side reactions. Additionally, composites of HEO with materials that possess good electrical conductivity and flexibility can enhance the electro-transport properties of the material,

mitigate volume changes during charge–discharge processes, prevent the detachment of active materials from current collectors, and thereby improve the material’s electrochemical lithium storage performance.

4. Materials and Methods

Preparation of $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$: $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$ nanoparticles were synthesized using the solution combustion method. Firstly, equimolar amounts (0.0025 mol) of metal nitrates (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were dissolved in 10 mL of deionized water. Next, 0.4692 g of glycine (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was added as fuel. The resulting solution was dried at 80 °C to obtain a gel. Subsequently, the gel was calcined in a tube furnace at 750 °C for 40 min and promptly removed from the furnace. This process yielded a powder composed of $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$ nanoparticles.

Material characterization: X-ray diffraction pattern of the samples was obtained using X-ray diffractometer (Bruker D2 Advance, Bruker, Lücken, Germany). The morphology was examined by scanning electron microscopy (SEM, Quanta 400, FEI, Waltham, Massachusetts, USA). Energy-dispersive spectroscopy (EDS) integrated into the SEM was employed to investigate the element distribution. The microstructure was observed using transmission electron microscopy (TEM, JEM-2010, JEOL, Tokyo, Japan). The composition and chemical states of the sample were investigated through X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, FEI, Waltham, Massachusetts, USA).

Electrochemical measurements: CR2032 half-cells were fabricated inside an argon-filled glove box (Dellix-S2100, Dellix Co., Ltd., Chengdu, Sichuan province, China), ensuring that oxygen and humidity levels were below 0.1 ppm. Working electrodes were prepared by casting a slurry containing 70 wt% of active materials, 20 wt% carbon black (C₄₅, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), and 10 wt% polyvinylidene fluoride (PVDF, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) onto Cu foils, followed by drying at 90 °C for 12 h under vacuum. A polypropylene membrane (Celgard 2400, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was employed as a separator. The electrolyte used was a mixture of dimethyl carbonate, ethylene carbonate, and methyl ethyl carbonate in a volume ratio of 1:1:1 with a 1 M LiPF₆ concentration. Charge–discharge measurements and rate measurements were carried out using a Neware battery testing system (CT4008, Neware, Shenzhen, China). Cyclic voltammetry (CV) tests were performed within a potential window of 0.01–3 V at a scan rate of 0.1 mV·s^{−1} on an electrochemical workstation (CHI660E, CH Instruments, Shanghai, China). In this process, the diameter of the pole piece was 14 mm and the average mass of active substance carried on each pole piece was 0.84 mg.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics12070198/s1>, Figure S1: XPS spectra of full spectra (a); Cr 2p (b); Mn 2p (c); Zn 2p (d); O 1s (e) before cycle and full spectra(f); Cr 2p(g); Mn 2p(h); Zn 2p(i); O 1s (j) after cycle.

Author Contributions: C.J. conceived the project. Y.W. (Yulong Wang), H.D., Y.W. (Yongxing Wei), R.N. and Z.J. carried out the experiments and analyzed the experimental data. Y.W. (Yulong Wang) and C.J. wrote the paper. Z.Y. participated in the analysis of experimental data and discussion of the results. C.J. and Q.D. revised the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding authors.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study.

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