

Article

Not peer-reviewed version

Rational design of Ni-doped V₂O₅@3D Ni core/shell composites for high-voltage and high-rate aqueous Zinc ion batteries

[Songhe Zheng](#) , Jianping Chen , Ting Wu , Ruimin Li , Xiaoli Zhao , [Yajun Pang](#) ^{*} , [Zhenghui Pan](#) ^{*}

Posted Date: 19 December 2023

doi: 10.20944/preprints202312.1364.v1

Keywords: ZIBs; Ni-V₂O₅; 3D Ni nanonets; Voltage window; Reaction kinetics



Preprints.org is a free multidiscipline platform providing preprint service that is dedicated to making early versions of research outputs permanently available and citable. Preprints posted at Preprints.org appear in Web of Science, Crossref, Google Scholar, Scilit, Europe PMC.

Copyright: This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Article

Rational Design of Ni-Doped V₂O₅@3D Ni Core/Shell Composites for High-Voltage and High-Rate Aqueous Zinc Ion Batteries

Songhe Zheng ^{1,*}, Ting Wu ^{1,*}, Jianping Chen ¹, Ruimin Li ¹, Xiaoli Zhao ^{1,*},
Yajun Pang ^{2,*} and Zhenghui Pan ^{1,*}

¹ School of Materials Science and Engineering, Tongji University, Shanghai 201804 China; zhengsh_crane@163.com; 2010448@tongji.edu.cn; 2331542@tongji.edu.cn; liruimin0187@link.tyut.edu.cn; zxl36@tongji.edu.cn

² College of Chemistry and Materials Engineering, Zhejiang A&F University, Hangzhou, 311300 China

* Correspondence: zxl63@tongji.edu.cn; yjpang@zafu.edu.cn; zhenghuipan@tongji.edu.cn

+ These authors contributed equally to this work

Abstract: Aqueous zinc ion batteries (ZIBs) have significant potential for large energy storage systems because of their high energy density, cost-effectiveness and environmental friendliness. However, the limited voltage window, poor reaction kinetics and structural instability of cathode materials are current bottlenecks, which contain the further development of ZIBs. In this work, we rationally design a Ni-doped V₂O₅@3D Ni core/shell composite on a carbon cloth electrode (Ni-V₂O₅@3D Ni@CC) by growing Ni-V₂O₅ on the free-standing 3D Ni metal nanonets for high-voltage and high-capacity ZIBs. Impressively, the embedded Ni doping increases the interlayer spacing of V₂O₅, extending the working voltage and improving zinc ion (Zn³⁰²⁺) reaction kinetics of the cathode materials; at the same time, the 3D structure with high specific surface area and superior electronic conductivity aid in fast Zn³⁰²⁺ transport. Consequently, the as-designed Ni-V₂O₅@3D Ni@CC cathodes can operate within a wide voltage window from 0.3 to 1.8 V vs. Zn₃₀/Zn³⁰²⁺ and deliver a high capacity of 270 mAh g⁻¹ (~ 1050 mAh cm⁻³) at a high current density of 0.8 A g⁻¹. In addition, the reversible Zn²⁺ (de)-incorporation reaction mechanisms in the Ni-V₂O₅@3D Ni@CC cathodes are investigated by multiple characterization methods (SEM, TEM, XRD, XPS, etc.). As a result, we achieved a big step toward practical applications of ZIBs.

Keywords: ZIBs; V₂O₅; 3D Ni nanonets; ion incorporation; voltage window; reaction kinetics; cycle stability

1. Introduction

Fossil fuels such as coal and oil play a crucial role in human activities. But the rapid reduction of these energy reserves and the environmental damage caused by their usage lead to an urgent energy revolution.[1] As a result, fossil fuels are gradually being replaced by clean energy in the application form of electricity. In the research field of electric energy storage systems, lithium-ion batteries (LIBs) have been developed for over 30 years, received in-depth research and achieved great success in commercial applications.[2] However, energy density limitation, high cost and environmental issues limit the further applications of LIBs.[3] To overcome these issues, researchers are exploring the feasibility of other active metals in energy storage devices to replace LIBs in the future.[4–6]

Among all the candidates, aqueous zinc-ion batteries (ZIBs) have received increasing attention as a promising candidate for large-scale energy storage devices due to the apparent advantages of using metallic Zn as the anode[7], including high theoretical capacity (5855 mAh cm^{-3})[8], low redox potential (-0.76 V *vs* standard hydrogen electrode, SHE)[9] and low-cost benefit from its vast reserve (the cost of Zn ($0.5\text{--}1.5 \text{ \$/lb}$) is much smaller than that of Li ($8\text{--}11 \text{ \$/lb}$)).[10] However, finding suitable cathode materials for high-performance ZIBs has become a top priority. Currently, manganese-, vanadium- and Prussian blue analogues (PBA)-based cathodes have been proven to be the typical cathode materials for ZIBs.[11] Among them, the manganese-[12–16] and PBA-based materials[17] have ideal charging and discharging platforms[18,19] but usually suffer from insufficient long-term cycling ability[20] and low reversible capacity[21–23] because of their intrinsic unstable structure characteristics.[24–28] Therefore, vanadium-based materials with high theoretical specific capacity and adjustable ion-transfer channels will most likely become promising candidates for high-performance cathodes in ZIBs.[29]

Generally, the narrow interlayer spacing[30] and poor electronic conductivity[31] of vanadium-based materials can lead to slow reaction kinetics and unstable structures during Zn^{2+} (de)-incorporation process, limiting their applications in ZIBs.[32] For this issue, the incorporation of metal ions, such as Na^+ , Li^+ , Mg^{2+} , Mn^{2+} , Cu^{2+} , *etc.*, [33–37] has been classified as one of the most effective strategies to enlarge interlayer spacing. Besides, metallic element incorporation adjusts the composition of V-based materials while changing their structures, and thus improves the electronic conductivity.[38–40] Therefore, this incorporation strategy significantly improves the materials' reaction kinetics from fastening both ion transportation and electron transportation. However, the insertion of metal ions may reduce the theoretical capacity of vanadium-based materials, especially during long-term cycle performance, due to the irreversible structure destruction, leading to a reduction of vanadium ion-storage.[41] Therefore, the influence of the type and the amount of pre-embedded metal ions should be considered when introducing metal ions into vanadium-based materials.[42] In addition, most reported cathode materials are in powder form. In order to be applied as cathodes, the powder must be stacked and bonded on a current collector, which not only blocks the active sites but also increase the “dead mass”, decreasing the energy density of ZIBs and causing an inevitable waste. In this regard, loading electrode active materials on 3D frameworks has been proven to be an effective strategy to avoid the use of adhesives and accumulation of active materials due to their large specific surface area and high porosity. Developing a solution to address both of these crucial problems simultaneously is highly effective yet challenging.

Herein, we propose a rational design of Ni-doped $\text{V}_2\text{O}_5@3\text{D Ni}$ core/shell composites on carbon cloth ($\text{Ni-V}_2\text{O}_5@3\text{D Ni@CC}$) for high-performance ZIBs. Specifically, 3D metallic Ni nanonets were grown on the surface of carbon cloth (CC). Compared with CC, Ni nanonets can be applied as a 3D framework to provide high electronic conductivity and larger surface area, for achieving higher quantity and full usage of active-material-loading. Besides, during the one-step- V_2O_5 loading process, metallic Ni particles were released from 3D nanonets and incorporated into V_2O_5 , modifying the interlayer structure of the active materials. As a result of this innovation, the as-obtained $\text{Ni-V}_2\text{O}_5@3\text{D Ni@CC}$ electrode can work in a wide voltage window[43] of 0.3 to 1.8 V versus Zn/Zn^{2+} and deliver a high capacity of 270 mAh g^{-1} ($\sim 1050 \text{ mAh cm}^{-3}$) at a current density of 0.8 mA g^{-1} . Moreover, multiple characterization methods are applied to investigate the reversible Zn^{2+} (de)-incorporation reaction

mechanism. Our strategy aims to broaden the application range to other materials and drive the practical commercial usage of ZIBs.

2. Experimental Section

Chemicals. Carbon cloth (1 cm × 2 cm), hexamethylenetetramine (HMT, C₆H₁₂N₄, 99%, Sinopharm Chemical Reagent Company Limited), nickel chloride hexahydrate (NiCl₂·6H₂O, 99%, Sigma-Aldrich), hydrogen peroxide solution (H₂O₂, 30%, Inan Mama Technology Company Limited), zinc sulfate (ZnSO₄·7H₂O, 99.5%, Sinopharm Chemical Reagent Company Limited), vanadium pentoxide (V₂O₅, Xiya Reagent) were used directly without any further purification.

Fabrication of Ni(OH)₂@CC. Firstly, the purchased CC was soaked in 5 M HCl aqueous solution to experience a complete cleaning, then washed in deionized (DI) water and pure ethanol, each for 15 min, in turn, to remove extra HCl. After that, CC was dried in air. Then the clean CC was cut into 1 cm × 2 cm pieces then used as a substrate to deposit Ni(OH)₂ on its surface. Clean CC was protected by ethoxylate except for an exposed area of 1 cm² on both sides. The Ni precursor solution was obtained by adding 0.125 mol NiCl₂·6H₂O and 0.25 mol HMT into 1 L DI water and experiencing a complete mixing. The CC substrate with an exposed area of 1 cm² mentioned before was immersed in 30 mL Ni precursor solution in a 50 mL glass beaker. The beaker was heated in an electric oven at 100 °C for 8 h to synthesize Ni(OH)₂ on CC. During this process, light green products are generally grown on the surface of CC. Finally, after being completely rinsed with distilled water and pure ethanol in turn for several times and dried in a vacuum oven for over 12 h, the Ni(OH)₂@CC samples were successfully fabricated.

Preparation of 3D Ni@CC. To obtain 3D Ni@CC, the fabricated Ni(OH)₂@CC samples were put into a porcelain boat, and then heated under an Ar/H₂ mixed atmosphere (the volume percent of H₂ is 5%) at 400 °C for 1 h. The temperature rising rate was set to 5 °C min⁻¹. During this process, Ni(OH)₂ was transferred into Ni. The 3D Ni@CC samples were obtained after being cooled to room temperature.

Preparation of Ni-V₂O₅@3D Ni@CC. The Ni-V₂O₅@3D Ni@CC electrode was prepared by a simple hydrothermal synthesis method. 0.91 g of divanadium pentaoxide was added into 40 mL of hydrogen peroxide solution. Subsequently, the above solution and 3D Ni@CC were transferred into a 100 mL Teflon-lined stainless-steel autoclave. After being sealed, these materials were heated under 180 °C and kept for 24 h. After cooling to room temperature, the autoclave was taken out, and the obtained samples were fully cleaned by ethanol, and then put into an oven to dry overnight at 80 °C. Then, the samples were annealed in air at 300 °C for 1 h at a heating rate of 2 °C min⁻¹ to get Ni-V₂O₅@3D Ni@CC. The mass loading of Ni-V₂O₅ is about 2.0 mg cm⁻².

Electrochemical measurements. All electrochemical performances of the samples were measured by a CHI 660C electrochemical workstation (CH Instruments Inc.). The Ni-V₂O₅@3D Ni@CC cathode performance in full-cell tests was investigated in the CR2025 coin cells. We chose glass microfiber (Whatman) as the separator and bare Zn foil (being washed by ethanol) as anode material. 2 M ZnSO₄ electrolyte was obtained by dissolving enough zinc sulfate into DI water. The assembling and testing process of coin cells were all experienced in an open atmosphere at a room temperature.

Characterization. Quanta 400 FEG scanning electron microscope (SEM) and a Tecnai G2 F20 S-Twin transmission electron microscope (TEM) were used to characterize microstructures of these samples. SEM was operated from 5.0-20.0 kV, and TEM was conducted at an accelerating voltage of 200 kV. The crystal structures of the samples were analyzed by X-ray diffraction (XRD) with a Bruker D8 diffractometer. The results of X-ray photoelectron spectroscopy (XPS) characterization were shown by an Axis Ultra DLD X-ray photoelectron spectroscopy and all data were referenced to the C 1s = 284.8 eV.

3. Results and Discussion

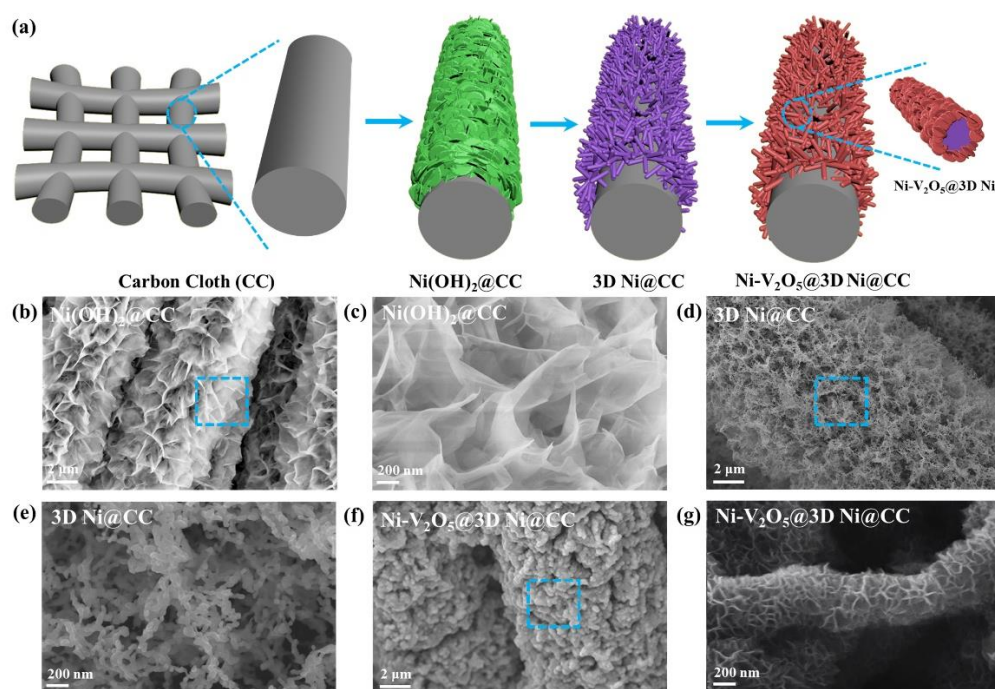


Figure 1. (a) Illustration of the preparation process of Ni-V₂O₅@3D Ni@CC electrode. (b-g) SEM images of (b-c) Ni(OH)₂ nanosheets synthesized on carbon cloth (CC), (d-e) 3D porous Ni nanonets on CC (3D Ni@CC) and (f-g) Ni-V₂O₅@3D Ni@CC.

The preparation process of the Ni-V₂O₅@3D Ni@CC electrode is illustrated in Figure 1a (the details can also be found in the experiment section) while scanning electron microscope (SEM) images during different steps can be seen in Figure 1b-g. CC has excellent characteristics including high electrical conductivity, remarkable structural flexibility and robust mechanical strength, which allows for its direct use as the current collector during this work. Besides, metal oxides/hydroxides can be easily grown on CC, therefore avoiding an extra usage of binder in the electrode fabrication process.[44] But CC still have an intrinsic shortage, which is the small surface area resulting in a low mass loading of active materials.[45] Therefore, to conquer this shortage, in the first step, Ni(OH)₂ nanosheets were grown on the CC surface. The SEM images of Ni(OH)₂@CC can be seen in Figure 2b-c, where the nanosheets were vertically grown on bare CC through immersion in the solution and experiencing the reaction between HMT and NiCl₂·6H₂O. We can see from the enlarged image that the large number of flexible Ni(OH)₂ nanosheets proved a much larger surface area in comparison with CC. Then the 3D metallic Ni nanonets (Figure 1a) were derived from the Ni(OH)₂ nanosheets by a reduction treatment under H₂ atmosphere. It can be seen that the obtained 3D metallic Ni nanonets still maintain a large surface area, and the morphology of Ni(OH)₂ transformed from nanosheets to well-dispersed and rob-shaped 3D nanosheets, offered a more sufficient space for active materials to load (Figure 1d-e). This 3D Ni@CC can serve as well as electrically conductive and stable supports for active materials, which is V₂O₅ in this research. Besides, Ni can act as incorporation ion to intercalate active material, changing internal structure, facilitating ion and electron transportation, making the oxidation-reduction reaction occur quickly. As for the Ni-pollution problem, it mainly refers to the environmental damage caused by the Ni metal smelting process. But in this research, raw material for synthesis Ni metal is environmentally friendly Ni(OH)₂, which is usually the product obtained from alkaline treatment of industrial wastewater containing Ni. Afterwards, nickel exists in its elemental form in the cathode of ZIBs, which is stable and easy to recycle, greatly reducing its bad impact on the environment.[46]

Then, after a simple hydrothermal synthesis method, V_2O_5 was grown on the surface of 3D Ni nanonets. The addition ratios of raw materials have experienced tests from low to high, to obtain the most suitable ratio between 3D Ni nanonets and $Ni-V_2O_5$, to maximize the usage of surface area, for a better electrochemical result. For example, the additive amount of $NiCl_2 \cdot 6H_2O$ was changed from 0.100 mol to 0.200 mol. As the amount continue increase, the final performance didn't improve and even deteriorated. We believe that this can be attributed to the continued growth of $Ni(OH)_2$, which finally led to heavier 3D Ni nanonets with smaller specific surface area, and easier to break down during the V_2O_5 loading process, which is a damage to the electrochemical performance of cathodes. And finally, we concluded that the ideal additive amount of $NiCl_2 \cdot 6H_2O$ is 0.125 mol.

The SEM image of as-synthesized $Ni-V_2O_5@3D Ni@CC$ demonstrates that V_2O_5 nanosheets were anchored homogeneously on the surface of the 3D Ni nanonets to form unique core-shell composites (Figure 1f-g). It should be noticed that during the V_2O_5 loading process, Ni atoms were released from Ni nanonets, achieving an incorporation to the interlayered V_2O_5 . The $Ni-V_2O_5@3D Ni@CC$ results in a higher energy density and transfer rate of ZIBs electrode while maintaining a high stability. More in-depth characterization of this part will be shown later.

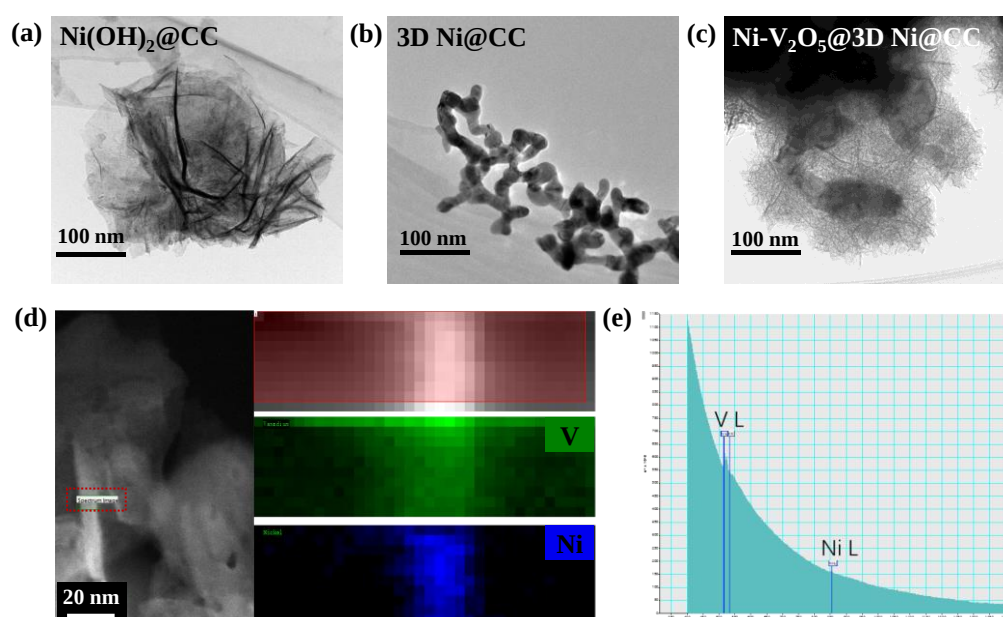


Figure 2. TEM images with higher magnification of (a) $Ni(OH)_2@CC$, (b) $3D Ni@CC$ and (c) $Ni-V_2O_5@3D Ni@CC$. (d) STEM image and elements distribution of a $Ni-V_2O_5$ nanosheet. (e) EELS result of $Ni-V_2O_5$ nanosheet taken from the red dashed box in Figure 2d.

We carried out a high-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) to further investigate the nanostructures of $Ni(OH)_2@CC$, $3D Ni@CC$ and $Ni-V_2O_5@3D Ni@CC$ samples (Figure 2a-c). From Figure 2a, we can see that abundant flexible $Ni(OH)_2$ nanosheets were well synthesized on CC. After a reduction process, the $Ni(OH)_2$ nanosheets were transferred into 3D metal Ni nanonets on the surface of CC, with a loose rod-shaped structure (Figure 2b). Finally, $Ni-V_2O_5$ nanosheets were grown on the Ni nanonets through a hydrothermal process. Through a higher resolution STEM image and elements characterization of $Ni-V_2O_5@3D Ni@CC$ (Figure 2c-d), not only robust V_2O_5 can be seen, but the incorporation of Ni element can be proved as well. There is an element distribution characterization of the sample in Figure 2d, in which bright parts represent areas with physical objects of $Ni-V_2O_5$ nanosheet. We selected a very small area from Figure 2d by using a red dashed box, called spectrum image to analyze its construction. The green pixels represent the V element, and the blue pixels represent the Ni element. It can be easily understood that due to the large mass loading of V_2O_5 fully covered 3D Ni nanonets, the V element is uniformly distributed on the sample, which reflected on the image are uniformly distributed green pixels. Blue pixels are also uniformly distributed on the image instead of concentrating on the area of

Ni nanonets, representing Ni achieved a good in-incorporation with V_2O_5 and a uniform distribution in it. In addition, electron energy loss spectroscopy (EELS) results from this area further demonstrate the occurrence of V_2O_5 growth and Ni incorporation (Figure 2e). EELS utilizes an incident electron beam to undergo inelastic scattering in the sample, and the energy loss of electrons directly reflects the mechanism of scattering, the chemical composition of the sample, and the thickness information. Therefore, it can analyze the elemental composition and other information from the analyzing area. Blue vertical lines in Figure 2e displayed different energy-loss caused by different elements, where two characteristic peaks belonging to V and Ni elements were detected, which is coordinated to the result from Figure 2d.

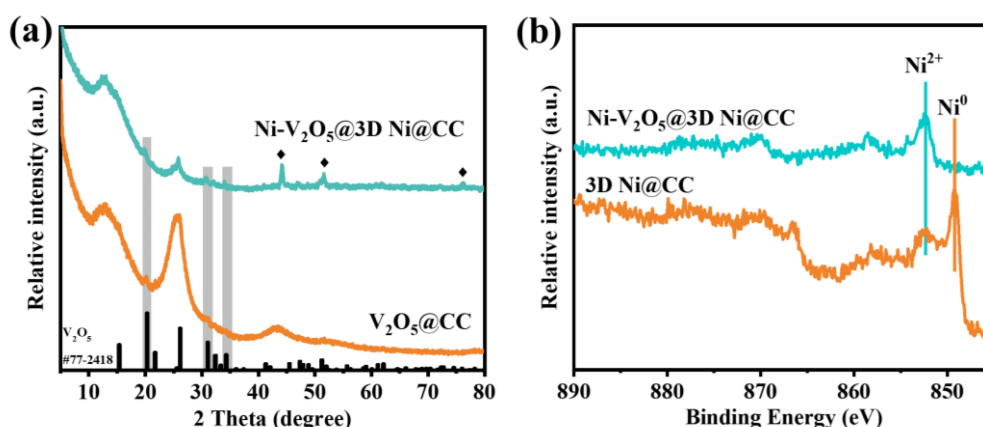


Figure 3. (a) XRD patterns of $V_2O_5@CC$ and $Ni-V_2O_5@3D Ni@CC$. (b) XPS spectra of $3D Ni@CC$ and $Ni-V_2O_5@3D Ni@CC$.

Apart from SEM and TEM images, our research also characterized the components and structures of samples through X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). As shown in Figure 3a and S1, XRD patterns of different samples can be indexed well to the $Ni(OH)_2$ (#38-0715), metallic Ni (#04-0850) and V_2O_5 (#77-2418), indicating that all these samples are well fabricated as expected. According to the XRD standard card of V_2O_5 (#77-2418), we choose three characteristic peaks (20.3° , 31.1° , 34.3°) to give an accurate description of the peaks shifting. In comparison with those characteristic peaks of pure $V_2O_5@CC$ sample (20.3° , 31.1° , 34.3°), the corresponding peaks of $Ni-V_2O_5@3D Ni@CC$ (19.8° , 30.7° , 34.0°) shift towards lower degrees, according to the Bragg equation: $2d \sin \theta = \lambda$ (d represents the distance between adjacent crystal layer, θ represents the angle between the incident X-ray and the crystal plane, λ It is the wavelength of X-ray), if the characteristic peak shifts towards a small angle while λ remains constant, d will be enlarged, representing a bigger interlayer space. It can be calculated through Bragg equation that the d -spaces have been enlarged for about $0.5 \text{ \AA}$. This evidence strongly proves that the interlayer spacing of the samples is enlarged due to the incorporation of Ni ion. In addition, the high-resolution XPS spectra of Ni element from $3D Ni@CC$ and $Ni-V_2O_5@3D Ni@CC$ were also presented in Figure 3b, further demonstrating the process of Ni ion incorporation. Clearly, in comparison with $3D Ni@CC$ sample, the Ni^0 of Ni element in the metallic nanonets sample disappeared and the main valence state became Ni^{2+} in $Ni-V_2O_5@3D Ni@CC$ (Figure 3b). Besides, according to the XPS spectra for V_2O_5 only vs. Ni incorporated V_2O_5 , there are shifts in the peak energies for vanadium and oxygen elements (Figure S2). Since Ni is incorporated within the interlayer spacing, it can be deduced that the intercalation of Ni not only changed the inner structure, but also affect the electronic environment of V and O, causing shifts in the binding energies. All these evidences indicated the occurrence of Ni incorporation, which is well consistent with the results from energy-dispersive spectroscopy (EDS) elemental mappings of SEM (Figure S3-4). It can be speculated that during the hydrothermal process for V_2O_5 loading, Ni^0 was released from Ni nanonets and transferred into Ni^{2+} , to incorporate with V_2O_5 , intercalating into its layered structure to achieve $Ni-V_2O_5$ and then grown on 3D nanonets. Therefore, the 3D Ni nanonets could not only serve as the framework for the better growth of V_2O_5

nanosheets but also participate in adjusting V_2O_5 layered structure. In other words, both the active site and spacing were enhanced for the diffusion of Zn^{2+} through such a facile one-step strategy.

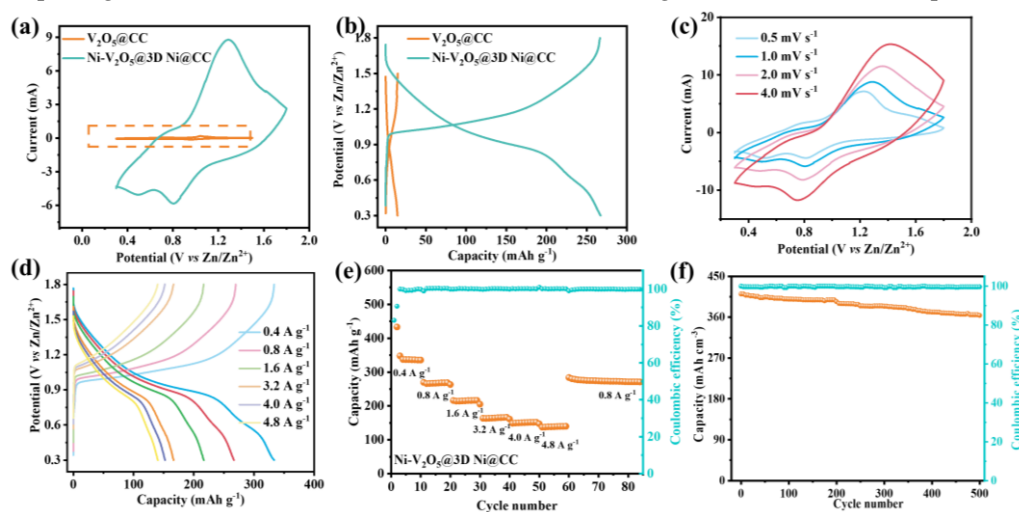


Figure 4. (a) CV curves of $\text{V}_2\text{O}_5@\text{CC}$ -based ZIB (0.3–1.5 V) and $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ -based ZIB (0.3–1.8 V) at a scan rate of 1.0 mV s^{-1} . (b) Galvanostatic charge-discharge (GCD) curves of $\text{V}_2\text{O}_5@\text{CC}$ -based ZIB and $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ -based ZIB under a current density of 0.8 A g^{-1} . (c) CV curves of $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ -based ZIB at different scan rates from 0.5 to 4.0 mV s^{-1} . (d) GCD curves of $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ -based ZIB under different current densities (0.4 – 4.8 A g^{-1}). (e) Rate capability test of $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ -based ZIB under various current densities (0.4 – 4.8 A g^{-1}). (f) Long-cycle stability test for $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ -based ZIB at a current density of 4.8 A g^{-1} .

The ZIBs were assembled by using metallic Zn as the anode to couple with $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ cathode or $\text{V}_2\text{O}_5@\text{CC}$ cathode (denoted as $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ -based ZIB or $\text{V}_2\text{O}_5@\text{CC}$ -based ZIB) and 2 M ZnSO_4 as an electrolyte. The corresponding electrochemical properties were also analyzed. The performance in oxygen evolution reaction (OER) activity is an important parameter for describing cathode stability in ZIBs. Higher reaction potential means the electrode material has a better stability during cycle performance. Meanwhile, a cathode material with higher OER potential can provide a wider voltage window for ZIBs, to realize a better performance closer to commercial usage. As it can be seen from Figure S5, during charging, there is a higher potential ($\sim 1.9 \text{ V}$) required for the $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ electrode to start decomposition and release oxygen, as the current density begins to increase rapidly. While $\text{V}_2\text{O}_5@\text{CC}$ only allows for a lower potential at about 1.6 V .

Then we carried out cyclic voltammetry (CV) curves at the scan rate of 1.0 mV s^{-1} . By comparing with pure $\text{V}_2\text{O}_5@\text{CC}$ -based ZIB (0.3–1.5 V), the $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ -based ZIB realizes a wider working potential window of 0.3–1.8 V, this can be attributed to the $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ electrode with a lower OER activity, as we have mentioned before. The wider voltage window enables the ZIBs to work at high energy density (Figure 4a, S6). In addition, we also note that this working potential window is larger than that of other recently reported V_2O_5 -based cathodes (e.g., $\text{Zn}_{0.25}\text{V}_2\text{O}_5$, $\text{Ca}_{0.25}\text{V}_2\text{O}_5$ and $\text{Na}_{0.33}\text{V}_2\text{O}_5$).[7,36,47,48]

Then, the galvanostatic charge-discharge (GCD) curves of $\text{V}_2\text{O}_5@\text{CC}$ -base ZIB and $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ -based ZIB under a current density of 0.8 A g^{-1} were carried out to compare the specific capacity (Figure 4b). Obviously, the $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ electrode delivers a much higher capacity than that of $\text{V}_2\text{O}_5@\text{CC}$. Besides, as for the $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ electrode, there's an obvious charge/discharge platform at about 1.2 V , which is obviously higher than that of the $\text{V}_2\text{O}_5@\text{CC}$ cathode. This is another powerful evidence to prove that the improved cathode material is more suitable for practical usage not only because of its high energy density and stability but also because of its wider working voltage window and higher working voltage platform, which is all better than that of $\text{V}_2\text{O}_5@\text{CC}$ electrode. Figure 4d shows the GCD curves of $\text{Ni-V}_2\text{O}_5@3\text{D Ni}@\text{CC}$ under various current densities (from 0.4 to 4.8 A g^{-1}), from which obvious charge and discharge plateaus can be discerned, consistent with the CV result (Figure 4c). During these two tests, it can be observed that

the working voltage platform is still maintained steadily ignoring the various changes of current density, proving that the Ni-V₂O₅@3D Ni@CC electrode is an ideal cathode material for ZIBs usage in different circumstances. It should be noticed that even though the voltage window seems to get smaller as the current density increases, this can be explained that the difference in CV curves is caused by capacity. The capacity of cathode materials always decreases under a faster voltage scan rate, since Zn ions can't be (de)intercalated completely. Therefore, the CV curve area is getting small, while the voltage window is remaining still actually.

In the rate performance tests, the Ni-V₂O₅@3D Ni@CC-based ZIB presents average discharge capacities of 330, 270, 216, 166, 152, and 140 mAh g⁻¹ at current densities of 0.4, 0.8, 1.6, 3.2, 4.0, and 4.8 A g⁻¹, respectively. Moreover, when the current density returns back to 0.8 A g⁻¹, the discharge capacity recovers to 270 mAh g⁻¹ (~1050 mAh cm⁻³), suggesting an excellent capability of rate performance. Meanwhile, the Ni-V₂O₅@3D Ni@CC all exhibits a high Coulombic efficiency (CE) at different current density from 0.4 to 4.8 A g⁻¹, then back to 0.8 A g⁻¹ (Figure 4e). In the long-cycle stability test, even under a high current density of 4.8 A g⁻¹, the Ni-V₂O₅@3D Ni@CC-based ZIB still maintains a nearly non-decreased 100% CE after cycling over 500 times with a specific capacity of about 110 mAh g⁻¹ (volume specific capacity of about 430 mAh cm⁻³, showed in Figure 4f). The performance reported here is better than that of other V₂O₅-based compounds such as V₂O₅/CC, V₂O₅/MXene, NH₄⁺-V₂O₅, V₂O₅/rGO *etc.* [5,6,49–54] Meanwhile, the smaller resistance of Ni-V₂O₅@3D Ni@CC-based ZIB in comparison with V₂O₅@CC-based ZIB proved by electrochemical impedance spectroscopy (EIS) test (can be seen in Figure S8) can well demonstrate that the incorporation of Ni in V₂O₅ active material not only benefits the energy storage performance and cycle stability but also improves the Zn²⁺ transport ability inside cathode, giving the Ni-V₂O₅@3D Ni@CC-based ZIB a better application potential. This can be explained that the incorporation of Ni ions not only enlarged the interlayer space of V₂O₅, allowing more Zn ions to intercalate, but also broadened Zn²⁺ ion transport channels, to fasten their moving speed inside electrode active material. Meanwhile, the broadened channels can escape from structure breakage during Zn²⁺ ion transportation and then improve the stability of the cathode during cycling.

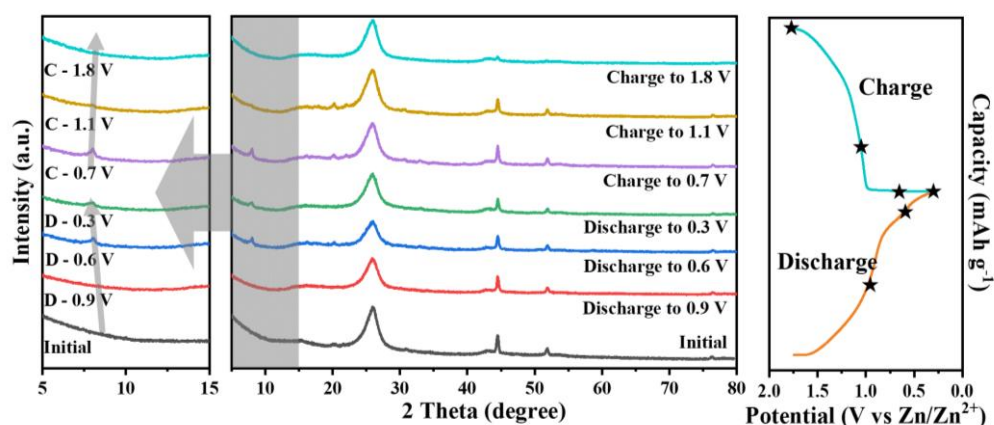


Figure 5. *Ex-situ* XRD patterns for Ni-V₂O₅@3D Ni@CC electrode during charge/discharge process under different potentials at a current density of 0.4 A g⁻¹.

In order to gain more insight into the (de)incorporation process of Zn²⁺ in the Ni-V₂O₅@3D Ni@CC-based ZIB, *ex-situ* XRD analysis was performed. As displayed in Figure 5, during the discharging process, there's a characteristic peak of the Ni-V₂O₅@3D Ni@CC electrode appeared on the position of 8.32°, representing an interlayer structure appearance due to the intercalation of Zn²⁺ ions inside the cathode. The characteristic peak shifted toward a lower angle (8.08° at 0.6 V) as the potential decreased until reaching the fully discharged state (7.92° at 0.3 V). During the charging process afterwards, the characteristic peak shifted back to the higher angles (8.04° at 0.7 V and 8.08° at 1.1 V), then disappeared again just like the beginning after being fully charged to 1.8 V. During the discharge process, Zn²⁺ ions are gradually intercalated into the cathode, resulting in a contraction of

interlayer spacing, which could be further recovered upon voltage reversal. This is strong evidence to prove that the energy storage mechanism of the Ni-V₂O₅@3D Ni@CC electrode is Zn²⁺ ions (de)intercalation. Meanwhile, the small shift of characteristic peaks represents a smaller interlayer-structure change during the charge/discharge process due to the existence of Ni ions, leading to a more stable cathode material.

4. Conclusions

In summary, we have designed Ni-doped V₂O₅@3D Ni core/shell composites on CC as an advanced cathode material for high-performance ZIBs. The 3D Ni nanonets with electronic conductivity composited on CC can provide a high specific surface area for V₂O₅ loading, which can conquer the inevitable shortage of CC. During the V₂O₅ loading process through a hydrothermal reaction, Ni atoms are transferred from Ni⁰ to Ni²⁺, and subsequently released from Ni nanonets to incorporate with V₂O₅. The intercalated Ni ions enlarged the interlayer space of the loaded V₂O₅, which is favourable for Zn²⁺ intercalation and transportation while maintaining its intrinsic structure. The as-prepared Ni-V₂O₅@3D Ni@CC electrode delivered a wide voltage window of 0.3 to 1.8 V versus Zn/Zn²⁺ and presented a high capacity of 270 mAh g⁻¹ at a current density of 0.8 mA g⁻¹. Moreover, even under a higher current density of 4.8 A g⁻¹, the Ni-V₂O₅@3D Ni@CC-based ZIB still maintains almost 100% CE after cycling over 500 times. Our research provides a new pathway to realize a better performance for V-based cathode materials and makes a big step toward the practical applications of commercial ZIBs. In further research, we can allocate more resources to systematically studying the usage of alternative materials and their impact on battery performance. This will allow us to obtain research results with reduced costs, simplified preparation methods, and increased practical value. The “3D metallic structure & incorporation” strategy can be expected to extend to other metals and electrode active materials, and cooperate with other improvement strategies including electrolyte and anode research areas on ZIBs, which will also favor the further design of high-performance ZIBs.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Figure S1: XRD patterns of Ni(OH)₂@CC and 3D Ni@CC; www.mdpi.com/xxx/s2 Figure S2: XPS spectra for 3D Ni@CC and Ni-V₂O₅@3D Ni@CC samples of (a) V and (b) O characteristic peaks; www.mdpi.com/xxx/s3 Figure S3: SEM image and corresponding elemental distribution of Ni-V₂O₅@3D Ni@CC; www.mdpi.com/xxx/s4 Figure S4: SEM image and corresponding elemental distribution of V₂O₅@CC; www.mdpi.com/xxx/s5 Figure S5: OER polarization curves of V₂O₅@CC and Ni-V₂O₅@3D Ni@CC; www.mdpi.com/xxx/s6 Figure S6. CV curves of V₂O₅@CC//Zn cell; www.mdpi.com/xxx/s7, Figure S7: EIS Nyquist plots for V₂O₅@CC//Zn and Ni-V₂O₅@3D Ni@CC//Zn cells.

Author Contributions: Conceptualization, Y.P. and Z.P.; methodology, T.W., S.Z.; validation, T.W., S.Z., J.C. and R.L.; writing-original draft preparation, S.Z.; writing-review and editing, X.Z., Y.P., Z.P.. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data used to support the findings of this study are available from the corresponding author upon request.

Acknowledgments: This work was supported by the Fundamental Research Funds for the Central Universities, conducted at Tongji University.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liu, H.; Wang, J.-G.; You, Z.; Wei, C.; Kang, F.; Wei, B., Rechargeable aqueous zinc-ion batteries: Mechanism, design strategies and future perspectives. *Materials Today* **2021**, *42*, 73-98.
2. Huang, M.; Wang, X.; Liu, X.; Mai, L., Fast Ionic Storage in Aqueous Rechargeable Batteries: From Fundamentals to Applications. *Advanced Materials* **2022**, *34*, (9).
3. Yan, J.; Ang, E. H.; Yang, Y.; Zhang, Y.; Ye, M.; Du, W.; Li, C. C., High-Voltage Zinc-Ion Batteries: Design Strategies and Challenges. *Advanced Functional Materials* **2021**, *31*, (22).

4. Song, J.; Xu, K.; Liu, N.; Reed, D.; Li, X., Crossroads in the renaissance of rechargeable aqueous zinc batteries. *Materials Today* **2021**, 45, 191-212.
5. Gourley, S. W.; Brown, R.; Adams, B. D.; Higgins, D. J. J., Zinc-ion batteries for stationary energy storage. *Joule* **2023**, 7, (7), 1415-1436.
6. Yang, X.; Gao, T.; Zhao, R.; Wu, Q.; Shi, K.; She, Z.; Lu, S.; Xie, Q.; Ruan, Y. J. E. T., Expanding Layer Spacing of Carbon-Coated Vanadium Oxide via Ammonium Ions for Fast Electrochemical Kinetics in Aqueous Zinc-Ion Batteries. *Energy Technology* **2023**, 11, (2), 2200990.
7. Li, Z.; Tan, J.; Wang, Y.; Gao, C.; Wang, Y.; Ye, M.; Shen, J., Building better aqueous Zn-organic batteries. *Energy & Environmental Science* **2023**, 16, (6), 2398-2431.
8. Zhao, Z.; Zhang, H.; Shi, X.; Zhang, Y.; Tang, C.; Zhao, H.; Liu, J.; Wang, G.; Li, L. J. S., Zincophilic Metal-Organic-Framework Interface Mitigating Dendrite Growth for Highly Reversible Zinc Metal Batteries. *Small* **2023**, 2304723.
9. Li, M.; Li, Z.; Wang, X.; Meng, J.; Liu, X.; Wu, B.; Han, C.; Mai, L., Comprehensive understanding of the roles of water molecules in aqueous Zn-ion batteries: from electrolytes to electrode materials. *Energy & Environmental Science* **2021**, 14, (7), 3796-3839.
10. Dong, H.; Li, J.; Guo, J.; Lai, F.; Zhao, F.; Jiao, Y.; Brett, D. J. L.; Liu, T.; He, G.; Parkin, I. P., Insights on Flexible Zinc-Ion Batteries from Lab Research to Commercialization. *Advanced Materials* **2021**, 33, (20).
11. Lin, Z.; Shi, H.-Y.; Lin, L.; Yang, X.; Wu, W.; Sun, X., A high capacity small molecule quinone cathode for rechargeable aqueous zinc-organic batteries. *Nature Communications* **2021**, 12, (1).
12. Zhao, J.; Xu, Z.; Zhou, Z.; Xi, S.; Xia, Y.; Zhang, Q.; Huang, L.; Mei, L.; Jiang, Y.; Gao, J.; Zeng, Z.; Tan, C., A Safe Flexible Self-Powered Wristband System by Integrating Defective MnO_{2-x} Nanosheet-Based Zinc-Ion Batteries with Perovskite Solar Cells. *ACS Nano* **2021**, 15, (6), 10597-10608.
13. Zhu, X.; Cao, Z.; Wang, W.; Li, H.; Dong, J.; Gao, S.; Xu, D.; Li, L.; Shen, J.; Ye, M., Superior-Performance Aqueous Zinc-Ion Batteries Based on the In Situ Growth of MnO₂ Nanosheets on V₂CTX MXene. *ACS Nano* **2021**, 15, (2), 2971-2983.
14. Cui, G.; Zeng, Y.; Wu, J.; Guo, Y.; Gu, X.; Lou, X. W., Synthesis of Nitrogen-Doped KMn₈O₁₆ with Oxygen Vacancy for Stable Zinc-Ion Batteries. *Advanced Science* **2022**, 9, (10).
15. Li, Y.; Li, X.; Duan, H.; Xie, S.; Dai, R.; Rong, J.; Kang, F.; Dong, L., Aerogel-structured MnO₂ cathode assembled by defect-rich ultrathin nanosheets for zinc-ion batteries. *Chemical Engineering Journal* **2022**, 441.
16. Ma, Y.; Xu, M.; Liu, R.; Xiao, H.; Liu, Y.; Wang, X.; Huang, Y.; Yuan, G., Molecular tailoring of MnO₂ by bismuth doping to achieve aqueous zinc-ion battery with capacitor-level durability. *Energy Storage Materials* **2022**, 48, 212-222.
17. Zeng, Y.; Lu, X. F.; Zhang, S. L.; Luan, D.; Li, S.; Lou, X. W., Construction of Co-Mn Prussian Blue Analog Hollow Spheres for Efficient Aqueous Zn-ion Batteries. *Angewandte Chemie International Edition* **2021**, 60, (41), 22189-22194.
18. Chen, C.; Shi, M.; Zhao, Y.; Yang, C.; Zhao, L.; Yan, C., Al-Intercalated MnO₂ cathode with reversible phase transition for aqueous Zn-Ion batteries. *Chemical Engineering Journal* **2021**, 422.
19. Cui, H.; Wang, T.; Huang, Z.; Liang, G.; Chen, Z.; Chen, A.; Wang, D.; Yang, Q.; Hong, H.; Fan, J.; Zhi, C., High-Voltage Organic Cathodes for Zinc-Ion Batteries through Electron Cloud and Solvation Structure Regulation. *Angewandte Chemie International Edition* **2022**, 61, (30).
20. Liu, L.; Wu, Y. C.; Huang, L.; Liu, K.; Duployer, B.; Rozier, P.; Taberna, P. L.; Simon, P., Alkali Ions Pre-Intercalated Layered MnO₂ Nanosheet for Zinc-Ions Storage. *Advanced Energy Materials* **2021**, 11, (31).
21. Islam, S.; Alfaruqi, M. H.; Putro, D. Y.; Park, S.; Kim, S.; Lee, S.; Ahmed, M. S.; Mathew, V.; Sun, Y. K.; Hwang, J. Y.; Kim, J., In Situ Oriented Mn Deficient ZnMn₂O₄@C Nanoarchitecture for Durable Rechargeable Aqueous Zinc-Ion Batteries. *Advanced Science* **2021**, 8, (4).
22. Deng, S.; Tie, Z.; Yue, F.; Cao, H.; Yao, M.; Niu, Z., Rational Design of ZnMn₂O₄ Quantum Dots in a Carbon Framework for Durable Aqueous Zinc-Ion Batteries. *Angewandte Chemie International Edition* **2022**, 61, (12).
23. Tang, H.; Chen, W.; Li, N.; Hu, Z.; Xiao, L.; Xie, Y.; Xi, L.; Ni, L.; Zhu, Y., Layered MnO₂ nanodots as high-rate and stable cathode materials for aqueous zinc-ion storage. *Energy Storage Materials* **2022**, 48, 335-343.
24. Liu, S.; Mao, J.; Pang, W. K.; Vongsvivut, J.; Zeng, X.; Thomsen, L.; Wang, Y.; Liu, J.; Li, D.; Guo, Z., Tuning the Electrolyte Solvation Structure to Suppress Cathode Dissolution, Water Reactivity, and Zn Dendrite Growth in Zinc-Ion Batteries. *Advanced Functional Materials* **2021**, 31, (38).
25. Ma, X.; Cao, X.; Yao, M.; Shan, L.; Shi, X.; Fang, G.; Pan, A.; Lu, B.; Zhou, J.; Liang, S., Organic-Inorganic Hybrid Cathode with Dual Energy-Storage Mechanism for Ultrahigh-Rate and Ultralong-Life Aqueous Zinc-Ion Batteries. *Advanced Materials* **2021**, 34, (6).
26. Moon, H.; Ha, K. H.; Park, Y.; Lee, J.; Kwon, M. S.; Lim, J.; Lee, M. H.; Kim, D. H.; Choi, J. H.; Choi, J. H.; Lee, K. T., Direct Proof of the Reversible Dissolution/Deposition of Mn²⁺/Mn⁴⁺ for Mild-Acid Zn-MnO₂ Batteries with Porous Carbon Interlayers. *Advanced Science* **2021**, 8, (6).
27. Wang, W.; Kale, V. S.; Cao, Z.; Lei, Y.; Kandambeth, S.; Zou, G.; Zhu, Y.; Abouhamad, E.; Shekhah, O.; Cavallo, L.; Eddaoudi, M.; Alshareef, H. N., Molecular Engineering of Covalent Organic Framework Cathodes for Enhanced Zinc-Ion Batteries. *Advanced Materials* **2021**, 33, (39).

28. Sambandam, B.; Mathew, V.; Kim, S.; Lee, S.; Kim, S.; Hwang, J. Y.; Fan, H. J.; Kim, J., An analysis of the electrochemical mechanism of manganese oxides in aqueous zinc batteries. *Chem* **2022**, 8, (4), 924-946.
29. Deka Boruah, B.; Mathieson, A.; Park, S. K.; Zhang, X.; Wen, B.; Tan, L.; Boies, A.; De Volder, M., Vanadium Dioxide Cathodes for High-Rate Photo-Rechargeable Zinc-Ion Batteries. *Advanced Energy Materials* **2021**, 11, (13).
30. Hu, L.; Wu, Z.; Lu, C.; Ye, F.; Liu, Q.; Sun, Z., Principles of interlayer-spacing regulation of layered vanadium phosphates for superior zinc-ion batteries. *Energy & Environmental Science* **2021**, 14, (7), 4095-4106.
31. Zhang, Z.; Xi, B.; Wang, X.; Ma, X.; Chen, W.; Feng, J.; Xiong, S., Oxygen Defects Engineering of $\text{VO}_2 \cdot x\text{H}_2\text{O}$ Nanosheets via In Situ Polypyrrole Polymerization for Efficient Aqueous Zinc Ion Storage. *Advanced Functional Materials* **2021**, 31, (34).
32. Wang, X.; Zhang, Z.; Xi, B.; Chen, W.; Jia, Y.; Feng, J.; Xiong, S., Advances and Perspectives of Cathode Storage Chemistry in Aqueous Zinc-Ion Batteries. *ACS Nano* **2021**, 15, (6), 9244-9272.
33. Cao, J.; Zhang, D.; Yue, Y.; Wang, X.; Pakornchote, T.; Bovornratanarak, T.; Zhang, X.; Wu, Z.-S.; Qin, J., Oxygen defect enriched $(\text{NH}_4)_2\text{V}_{10}\text{O}_{25} \cdot 8\text{H}_2\text{O}$ nanosheets for superior aqueous zinc-ion batteries. *Nano Energy* **2021**, 84.
34. Li, R.; Xing, F.; Li, T.; Zhang, H.; Yan, J.; Zheng, Q.; Li, X., Intercalated polyaniline in V_2O_5 as a unique vanadium oxide bronze cathode for highly stable aqueous zinc ion battery. *Energy Storage Materials* **2021**, 38, 590-598.
35. Pan, Z.; Liu, X.; Yang, J.; Li, X.; Liu, Z.; Loh, X. J.; Wang, J., Aqueous Rechargeable Multivalent Metal-Ion Batteries: Advances and Challenges. *Advanced Energy Materials* **2021**, 11, (24).
36. Du, Y.; Wang, X.; Zhang, Y.; Zhang, H.; Man, J.; Liu, K.; Sun, J., High mass loading CaV_4O_9 microflowers with amorphous phase transformation as cathode for aqueous zinc-ion battery. *Chemical Engineering Journal* **2022**, 434.
37. Feng, Z.; Zhang, Y.; Sun, J.; Liu, Y.; Jiang, H.; Cui, M.; Hu, T.; Meng, C., Dual ions enable vanadium oxide hydration with superior Zn^{2+} storage for aqueous zinc-ion batteries. *Chemical Engineering Journal* **2022**, 433.
38. Wang, X.; Naveed, A.; Zeng, T.; Wan, T.; Zhang, H.; Zhou, Y.; Dou, A.; Su, M.; Liu, Y.; Chu, D., Sodium ion stabilized ammonium vanadate as a high-performance aqueous zinc-ion battery cathode. *Chemical Engineering Journal* **2022**, 446.
39. Yang, W.; Yang, Y.; Yang, H.; Zhou, H., Regulating Water Activity for Rechargeable Zinc-Ion Batteries: Progress and Perspective. *ACS Energy Letters* **2022**, 7, (8), 2515-2530.
40. Zhang, R.; Liang, P.; Yang, H.; Min, H.; Niu, M.; Jin, S.; Jiang, Y.; Pan, Z.; Yan, J.; Shen, X.; Wang, J., Manipulating intercalation-extraction mechanisms in structurally modulated $\delta\text{-MnO}_2$ nanowires for high-performance aqueous zinc-ion batteries. *Chemical Engineering Journal* **2022**, 433.
41. Peng, Y.; Xu, J.; Xu, J.; Ma, J.; Bai, Y.; Cao, S.; Zhang, S.; Pang, H., Metal-organic framework (MOF) composites as promising materials for energy storage applications. *Advances in Colloid and Interface Science* **2022**, 307.
42. Xing, Z.; Xu, G.; Han, J.; Chen, G.; Lu, B.; Liang, S.; Zhou, J., Facing the capacity fading of vanadium-based zinc-ion batteries. *Trends in Chemistry* **2023**, 5, (5), 380-392.
43. Chen, Z.; Cui, H.; Hou, Y.; Wang, X.; Jin, X.; Chen, A.; Yang, Q.; Wang, D.; Huang, Z.; Zhi, C., Anion chemistry enabled positive valence conversion to achieve a record high-voltage organic cathode for zinc batteries. *Chem* **2022**, 8, (8), 2204-2216.
44. Xiao, X.; Zheng, Z.; Zhong, X.; Gao, R.; Piao, Z.; Jiao, M.; Zhou, G., Rational Design of Flexible Zn-Based Batteries for Wearable Electronic Devices. *ACS Nano* **2023**, 17, (3), 1764-1802.
45. Paul, R.; Zhai, Q.; Roy, A. K.; Dai, L. J. I. M., Charge transfer of carbon nanomaterials for efficient metal-free electrocatalysis. **2022**, 1, (1), 28-50.
46. Wang, Y.; Song, J.; Wong, W. Y., Constructing 2D Sandwich-like MOF/MXene Heterostructures for Durable and Fast Aqueous Zinc-Ion Batteries. *Angewandte Chemie International Edition* **2023**, 62, (8).
47. Zong, Q.; Wang, Q.; Liu, C.; Tao, D.; Wang, J.; Zhang, J.; Du, H.; Chen, J.; Zhang, Q.; Cao, G., Potassium Ammonium Vanadate with Rich Oxygen Vacancies for Fast and Highly Stable Zn-Ion Storage. *ACS Nano* **2022**, 16, (3), 4588-4598.
48. Liu, Y.; Liu, Y.; Wu, X., Defect engineering of vanadium-based electrode materials for zinc ion battery. *Chinese Chemical Letters* **2023**, 34, (7).
49. Gao, F.; Mei, B.; Xu, X.; Ren, J.; Zhao, D.; Zhang, Z.; Wang, Z.; Wu, Y.; Liu, X.; Zhang, Y., Rational design of ZnMn_2O_4 nanoparticles on carbon nanotubes for high-rate and durable aqueous zinc-ion batteries. *Chemical Engineering Journal* **2022**, 448.
50. Li, X.; Ma, Y.; Yue, Y.; Li, G.; Zhang, C.; Cao, M.; Xiong, Y.; Zou, J.; Zhou, Y.; Gao, Y., A flexible Zn-ion hybrid micro-supercapacitor based on MXene anode and V_2O_5 cathode with high capacitance. *Chemical Engineering Journal* **2022**, 428.

51. Sun, R.; Guo, X.; Dong, S.; Wang, C.; Zeng, L.; Lu, S.; Zhang, Y.; Fan, H., Zn₃V₃O₈@ZnO@NC heterostructure for stable zinc ion storage from assembling nanodisks into cross-stacked architecture. *Journal of power sources* **2023**, 567.
52. Wang, T.; Li, S.; Weng, X.; Gao, L.; Yan, Y.; Zhang, N.; Qu, X.; Jiao, L.; Liu, Y., Ultrafast 3D Hybrid-Ion Transport in Porous V₂O₅ Cathodes for Superior-Rate Rechargeable Aqueous Zinc Batteries. *Advanced Energy Materials* **2023**, 13, (18).
53. Zhao, D.; Wang, X.; Zhang, W.; Zhang, Y.; Lei, Y.; Huang, X.; Zhu, Q.; Liu, J., Unlocking the Capacity of Vanadium Oxide by Atomically Thin Graphene-Analogous V₂O₅·nH₂O in Aqueous Zinc-Ion Batteries. *Advanced Functional Materials* **2023**, 33, (13).
54. Zhang, L.; Zhu, J.; Li, X.; Mu, S.; Verpoort, F.; Xue, J.; Kou, Z.; Wang, J. J. I. M., Nurturing the marriages of single atoms with atomic clusters and nanoparticles for better heterogeneous electrocatalysis. **2022**, 1, (1), 51-87.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.