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Novel $NH_4V_4O_{10}$-Redox Graphene Oxide Cathodes for Zinc-Ion Batteries: Theoretical Predictions and Experimental Validation

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Abstract: This investigation explores the potential of enhancing aqueous zinc-ion batteries (AZIBs) through the introduction of a novel cathode material, $NH_4V_4O_{10}$ (NVO), combined with redox graphene oxide (rGO). Utilizing Density Functional Theory (DFT), it was hypothesized that the incorporation of rGO would increase the interlayer spacing of NVO and diminish the charge transfer interactions, thus promoting enhanced diffusion of Zn^{2+} ions. These theoretical predictions were substantiated by experimental data acquired from hydrothermal synthesis, which indicated a marked increase in interlayer spacing. Significantly, the NVO-rGO composite exhibits remarkable cyclic durability, maintaining 94.54% of its initial specific capacity of 506.9 mAh g^{-1} after 600 cycles at a current density of 5 A g^{-1}. The electrochemical performance of NVO-rGO not only surpasses that of pristine NVO but also outperforms the majority of existing vanadium oxide cathode materials reported in the literature. This study underscores the effective integration of theoretical insights and experimental validation, contributing to the advancement of high-performance energy storage technologies.

Keywords: zinc-ion batteries; cathode materials; $NH_4V_4O_{10}$; redox graphene oxide

1. Introduction

As global fossil fuel reserves continue to deplete, there is an urgent need to transition towards more sustainable energy infrastructures, emphasizing the harnessing of renewable energy sources such as wind and tidal energy [1,2]. A predominant challenge with these renewables is their inherent intermittency, which necessitates the development of efficient energy storage solutions—a critical topic in current scientific discourse. Over the past decade, lithium-ion batteries (LIBs) have become a central technology in this field, attracting significant interest due to their high energy density and commendable cycle life [3,4], thus establishing their dominance in the domain of electrochemical energy storage. However, concerns about the limited availability of lithium, rising costs, and potential safety risks associated with organic electrolytes have been highlighted [5,6]. As a result, there is an increasing focus among researchers on exploring alternative battery technologies that offer ecological sustainability, cost-effectiveness, and inherent safety.

In the evaluation of diverse battery technologies, aqueous zinc-ion batteries (AZIBs) have emerged as a notable contender. Their increasing prominence is attributed to several advantageous attributes: abundant global zinc reserves, the environmentally benign nature of its utilization, a commendable theoretical specific capacity of 820 mAh g^{-1}, and a favorable redox potential of −0.76 V versus the Standard Hydrogen Electrode (SHE) [7,8]. Despite these advantages, the technology faces significant challenges. A primary issue is the pronounced electrostatic interactions between Zn^{2+} ions and electrode materials [9]. These interactions create substantial potential energy barriers during the intercalation and de-intercalation of Zn^{2+} ions, leading to structural degradation in cathode materials through repeated charge-discharge cycles [10].

The cathode plays a crucial role in determining the electrochemical performance of batteries, particularly in the case of aqueous zinc-ion batteries (AZIBs). Consequently, developing high-performance cathode materials that facilitate rapid Zn^{2+} migration and exhibit high capacity is essential for the practical implementation of AZIBs. A variety of cathode materials, including manganese (Mn)-based [11–13], vanadium (V)-based compounds [14,15], and Prussian blue analogs [16,17], have been extensively investigated. Among these, vanadium-based oxides are distinguished by their range of oxidation states from V^{2+} to V^{5+}. This variability in oxidation states provides greater structural and coordination flexibility, and the possibility for multi-electron transfer, which can lead to enhanced specific capacities [18]. However, the diversity of these oxidation states also presents challenges, including slow reaction kinetics and complex reaction mechanisms that can hinder performance.

Despite these challenges, AZIBs exhibit considerable potential and promise for future energy storage systems. Nonetheless, widespread practical application requires ongoing research to overcome the aforementioned obstacles. V_2O_5, a well-known layered vanadium-based cathode material, demonstrates excellent electrochemical performance. Its derivative, $NH_4V_4O_{10}$ (NVO), not only retains the benefits of V_2O_5 but also enhances the stability of the layered structure through the formation of N-H-O hydrogen bonds between the $[VO_6]$ octahedra [19–23].

Despite these promising attributes, the cyclic and rate performances of NVO remain less than optimal. Density Functional Theory (DFT) calculations indicate that incorporating redox graphene oxide (rGO) with NVO can enhance the interlayer spacing of the material. Additionally, rGO serves a protective role, reducing the charge transfer interactions between Zn^{2+} ions and the vanadium oxide matrix, thus facilitating improved Zn^{2+} diffusion. Following these theoretical predictions, NVO was composited with rGO using a hydrothermal synthesis method. The experimental results confirmed the theoretical predictions, showing an increase in interlayer spacing. At a current density of 0.2 A g^{-1}, the initial specific capacity was recorded at 506.9 mAh g^{-1}. Remarkably, after enduring 600 cycles at an elevated current density of 5 A g^{-1}, the composite material maintained 94.54% of its initial capacity.

2. Results and Discussion

2.1. DFT Calculations

In order to investigate the effects of rGO composite on the NVO system, we conducted a series of Density Functional Theory (DFT) calculations. We constructed models for Zn^{2+} embedded in pristine NVO (Zn-NVO) and Zn^{2+} embedded in an NVO system composited with rGO (Zn-NVO@rGO). Both systems were subjected to stringent structural optimizations, the outcomes of which are illustrated in Figure 1a,c, respectively. These figures highlight the expansion in interlayer spacing subsequent to the incorporation of rGO, which facilitates the diffusion of Zn^{2+} ions.

To further examine the specifics of Zn charge transfer, we calculated the charge density difference, as depicted in Figure 1b,d. In these visual representations, blue regions denote areas where charge density around Zn^{2+} has decreased, whereas yellow regions indicate an increase in charge density. It is important to note that in the pristine NVO system, there is a discernible charge transfer between Zn^{2+} and the oxygen atoms in the V-O bonds across two distinct layers. This transfer results in strong electrostatic interactions between Zn^{2+} and the host material, which hinders the diffusion of Zn^{2+} ions.

However, the introduction of rGO significantly alters this dynamic. rGO serves as a shielding layer, reducing the extent of charge transfer to only the oxygen in the V-O bonds of one layer of the NVO system. This reduction in charge transfer weakens the electrostatic interactions between Zn^{2+} and the vanadium oxide host, thereby promoting the diffusion of Zn^{2+} ions and enhancing the electrochemical performance of the Zn-NVO@rGO system. These DFT calculations are instrumental in providing a microscopic view of the electronic interactions and structural changes induced by the addition of rGO.

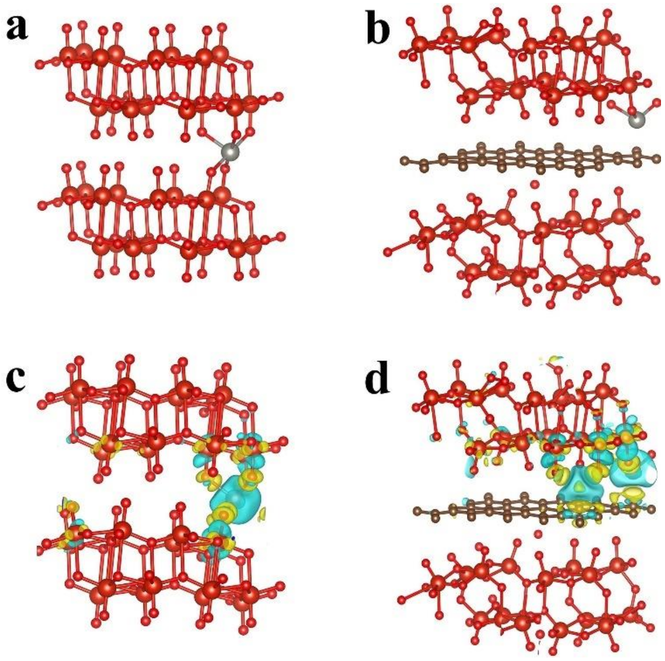

Figure 1. Optimized structure of (**a**) Zn-NVO and (**b**) Zn-NVO@rGO, charge density difference of (**c**) Zn-NVO and (**d**) Zn-NVO@rGO.

2.2. Morphological Characterization

To validate the results obtained from DFT calculations, we synthesized NVO and NVO@rGO using a single-step hydrothermal method. To ascertain the structural composition of these materials, X-ray Powder Diffraction (XRD) analysis was performed. The XRD patterns, presented in Figure 2a, show that the diffraction peaks of NVO@rGO align well with the standard card for $NH_4V_4O_{10}$ [JCPDS 31-0075], with characteristic peaks at 7.44°, 25.06°, 30.32°, 45.84°, and 48.6° corresponding to standard NVO peaks. The synthesized NVO also matched the standard $NH_4V_4O_{10}$ card accurately. Significantly, compared to pristine NVO and the standard card, the (001) plane peak of NVO@rGO exhibited a shift towards lower angles, from 9.6 Å to 11.87 Å. This increase in interlayer spacing corresponds with our DFT predictions. The shift to lower angles and the resulting expansion in interlayer spacing suggest enhanced intercalation capability and potentially improved ion diffusion pathways, which are critical for the electrochemical performance of the composite material.

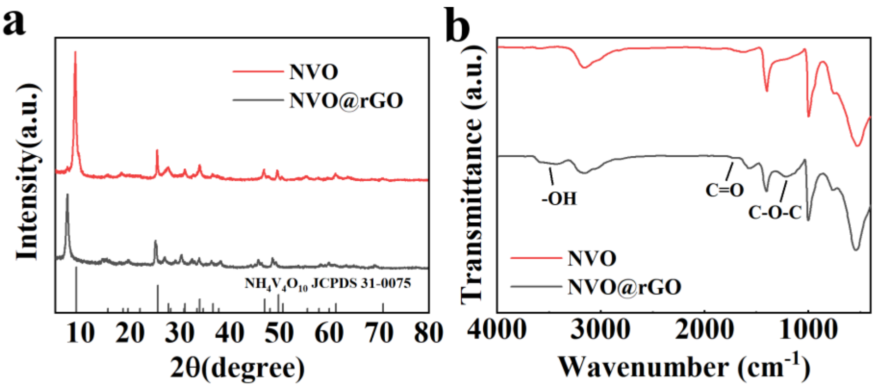

Figure 2. (**a**) XRD patterns and (**b**) FTIR spectrum of NVO, NVO@rGO.

In addition to X-ray diffraction, Fourier Transform Infrared Spectroscopy (FTIR) was employed to further investigate the structural composition of NVO and NVO@rGO. As depicted in Figure 2b, both materials exhibited similar FTIR spectra, indicating a preservation of the base structural features upon rGO integration. However, the spectrum for NVO@rGO displayed several additional, albeit weaker, absorption peaks that are characteristic of rGO functional groups. Specifically, the absorption peak at 3436 cm^{-1} is attributed to the stretching vibrations of –OH groups, indicative of residual hydroxyl functionalities or absorbed water molecules. The peak at 1728 cm^{-1} corresponds to the C=O stretching vibrations, typically found in carboxylic acid groups or ketones, while the peak at 1222 cm^{-1} represents the C–O–C vibrations, which are commonly associated with ethers or esters. The relative weakness of these oxygen-containing functional group peaks suggests incomplete reduction of the graphene oxide to rGO

Scanning Electron Microscopy (SEM) was utilized to investigate the microstructural morphology and elemental composition of the synthesized NVO@rGO composite. Images presented in Figure 3a,b reveal that NVO@rGO consists of uniform ultrathin nanosheets. The ultrathin structure is advantageous for enhancing the surface area available for electrochemical reactions and facilitates rapid ion transport.

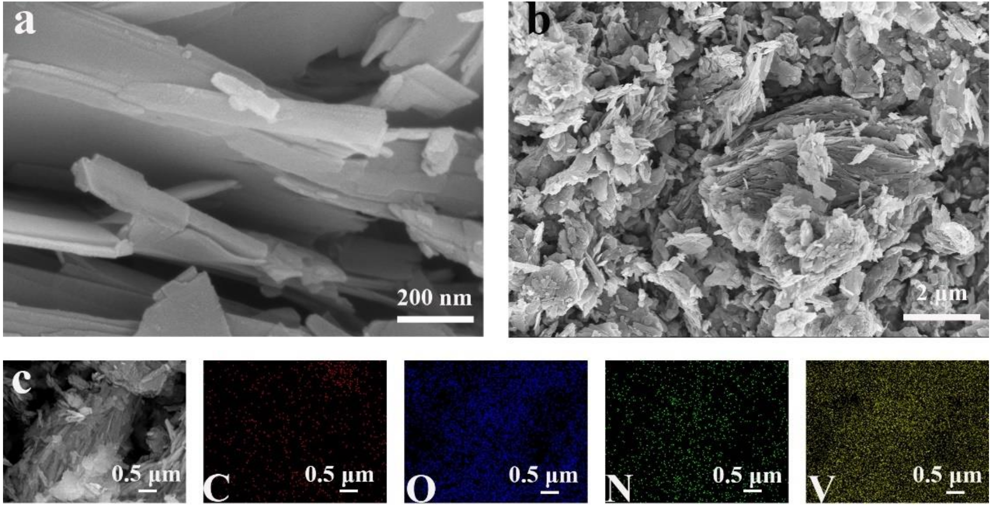

Figure 3. (**a**,**b**) SEM patterns of NVO@rGO; (**c**) EDS mapping of NVO@rGO.

Further analysis using SEM Energy-Dispersive X-ray Spectroscopy (EDS) mapping (shown in Figure 3c) confirmed the homogeneous distribution of carbon (C), oxygen (O), nitrogen (N), and vanadium (V) elements within the composite. The presence of these elements in a uniformly distributed manner indicates effective incorporation of rGO into the NVO matrix. This homogeneous distribution is crucial for ensuring consistent electrochemical behavior across the material, which is essential for the stability and reliability of battery performance.

To gain further insight into the microstructural details of NVO@rGO, Transmission Electron Microscopy (TEM) was employed. The TEM images, as shown in Figures 4a,b, distinctly reveal the nanosheet morphology of the composite. These images also clearly demonstrate the uniform coating of rGO on the NVO cathode material. The high-resolution TEM (HRTEM) images, displayed in Figure 4c, distinctly show the lattice fringes of NVO@rGO, with a lattice spacing of 0.198 nm that corresponds to the (–205) plane of NVO. This precise observation of lattice fringes underscores the crystalline nature of the NVO within the composite and supports the structural integrity of the material even after the incorporation of rGO.

Furthermore, the Selected Area Electron Diffraction (SAED) patterns, presented in Figure 4d, exhibit a ring-like diffraction pattern typical of polycrystalline materials. This pattern clearly resolves the diffraction rings corresponding to the (400), (001), and (110) planes of NVO, indicating that the crystalline phases of NVO are well-preserved within the composite. The presence of these distinct diffraction rings also helps confirm the phase purity and crystalline quality of the material, which are essential for predictable and stable electrochemical performance.

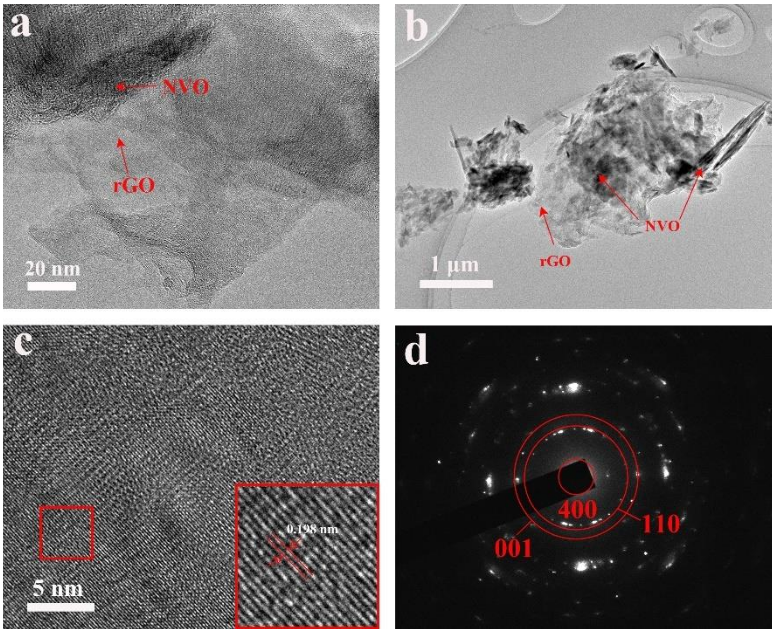

Figure 4. (**a**,**b**) TEM images, (**c**) lattice fringes and (**d**) SAED patterns of NVO@rGO.

2.3. Electrochemical Properties Characterization

To evaluate the electrochemical behavior of NVO@rGO in reaction processes, the material was assembled into a coin cell for electrochemical performance testing. Cyclic voltammetry (CV) scans were initially performed at a scan rate of 0.1 mV s^{-1} (illustrated in Figure 5a), where the good overlap of the first four cycles indicated excellent cyclic stability. The presence of multiple oxidation and reduction peaks within these curves confirmed that the electrochemical reactions of NVO@rGO are complex and involve multiple steps. Specifically, the oxidation and reduction peaks at 1.499 V and 1.344 V respectively, are associated with the intercalation and deintercalation of NH_4^+ ions [24–26], highlighting the active role of ammonium in the electrochemical process.

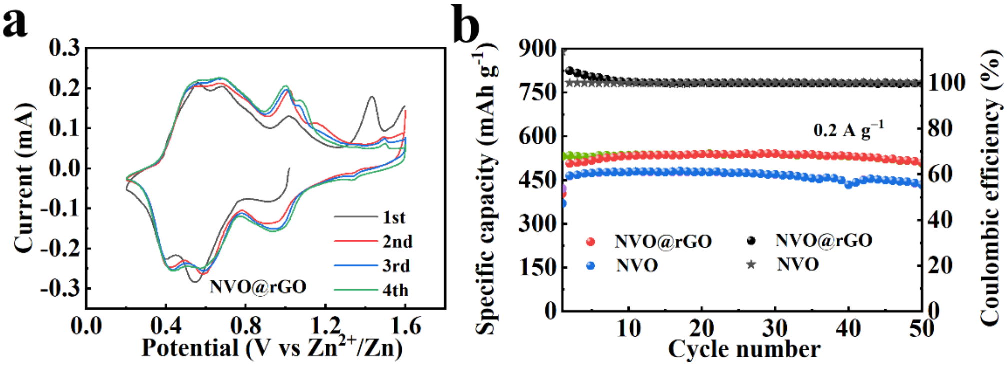

Figure 5. (**a**) CV curves of NVO@rGO; (**b**) Cycling performance plots of NVO and NVO@rGO at a current density of 0.2 A g^{-1}.

Subsequently, the cycling performance of both NVO and NVO@rGO was tested at a current density of 0.2 A g^{-1} (shown in Figure 5b). The initial specific capacity of NVO was recorded at 464.4 mAh g^{-1}, with a capacity retention of 93.49% after 50 cycles. In comparison, NVO@rGO exhibited a higher initial capacity of 506.9 mAh g^{-1} and an exceptional capacity retention of 100.4% after the same number of cycles. This improvement in both initial capacity and retention for NVO@rGO compared to pristine NVO is a testament to the beneficial effects of rGO integration, which enhances the structural stability and electrochemical reactivity of the material. These results are in line with the

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predictions from DFT calculations, which suggested that the addition of rGO would facilitate better ion diffusion and charge transfer.

Moreover, the performance of NVO@rGO not only surpasses that of pristine NVO but also exceeds most of the vanadium oxide cathode materials reported in current literature (as shown in Table 1). This superior performance can be attributed to the structural and electronic enhancements brought about by the incorporation of rGO into the NVO matrix, which optimize the material's electrochemical properties.

Table 1. Comparison with reported electrochemical properties of vanadium oxidation chemicals.

Cathode materials	Electrochemical performance (Capacity retention, cycle numbers)	Reference
NVO@rGO	506.9mAh g^{-1} at 0.2 A g^{-1} (100%, 50 cycles)	This work
$(NH_4)_{0.37}V_2O_5{\cdot}0.15H_2O$	398 mAh g^{-1} at 0.5 A g^{-1} (90%, 50 cycles)	[26]
$KNH_4V_4O_{10}$	405 mAh g^{-1} at 0.4 A g^{-1} (92.1%, 100 cycles)	[27]
Cs-V_2O_5	368.5 mAh g^{-1} at 0.1 A g^{-1} (90%, 200 cycles)	[28]
$(NH_4)_xV_2O_5{\cdot}nH_2O$	372 mAh g^{-1} at 0.1 A g^{-1} (63%, 50 cycles)	[29]
$Zn_3V_2MoO_8$	336.7 mAh g^{-1} at 0.2 A g^{-1} (90%, 70 cycles)	[30]
$NaCaV_2O_5$	310 mAh g^{-1} at 0.5A g^{-1} (100%, 200 cycles)	[31]
$(NH_4)_2V_4O_9$	493 mAh g^{-1} at 0.2 A g^{-1} (83.2%, 100 cycles)	[32]
V_3O_7/V_6O_{13}	415 mAh g^{-1} at 0.1 A g^{-1} (73%, 100 cycles)	[33]
$Na_2V_6O_{16}{\cdot}3H_2O$	401.1 mAh g^{-1} at 0.3 A g^{-1} (91.8%, 300 cycles)	[34]
O_d-HNaVO@rGO	380.4 mAh g^{-1} at 0.5 A g^{-1} (97.4%, 200 cycles)	[35]

Figure 6 presents the galvanostatic charge-discharge (GCD) curves for NVO@rGO and NVO at a current density of 0.2 A g^{-1}. The curves exhibit similar shapes, indicating analogous electrochemical processes are underway in both samples. The high degree of overlap in the GCD curves suggests that both materials, NVO@rGO and NVO, exhibit excellent cyclic stability. This similarity in electrochemical behavior can be attributed primarily to the inherent properties of NVO in both cases.

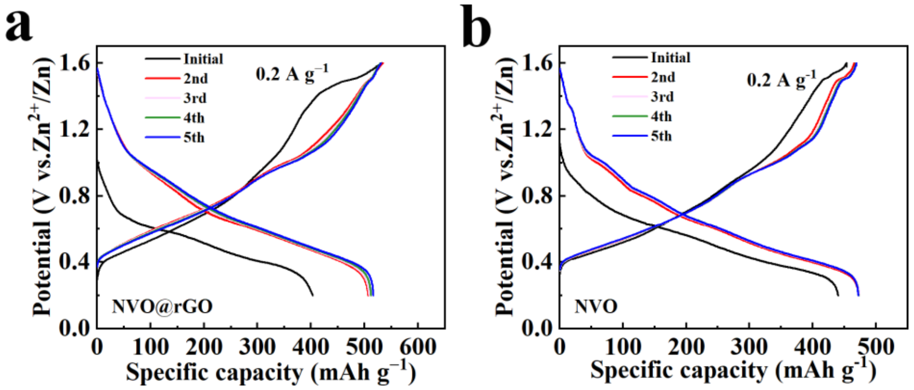

Figure 6. GCD curves of (**a**) NVO@rGO and (**b**) NVO at a current density of 0.2 A g^{-1}.

Figure 7 showcases the rate performance of NVO@rGO compared to NVO, as the current density was increased stepwise from 0.2 A g^{-1} to 5 A g^{-1}. The specific capacities for NVO@rGO at these current densities were recorded at 494.8, 494.4, 491.4, 470.4, and 401.4 mAh g^{-1} respectively. Notably, when the current density was reverted back to 0.2 A g^{-1}, the specific capacity of NVO@rGO impressively recovered to 518.3 mAh g^{-1}. This recovery and the overall higher capacities at each rate compared to NVO underscore the superior rate capability and resilience of the composite material.

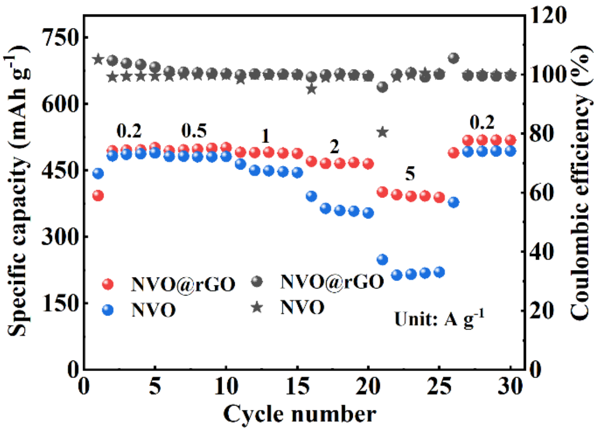

Figure 7. Rate performance graph of NVO@rGO and NVO.

The enhanced performance of NVO@rGO can be attributed to the incorporation of rGO, which not only improves the electrical conductivity of NVO but also serves as a structural scaffold. This scaffold helps in stabilizing the crystal structure of NVO during electrochemical cycling, mitigating volume expansion that often leads to rapid capacity fade in such materials. Additionally, the presence of rGO likely facilitates better electron and ion transport within the electrode, enhancing both the rate capability and cycling stability.

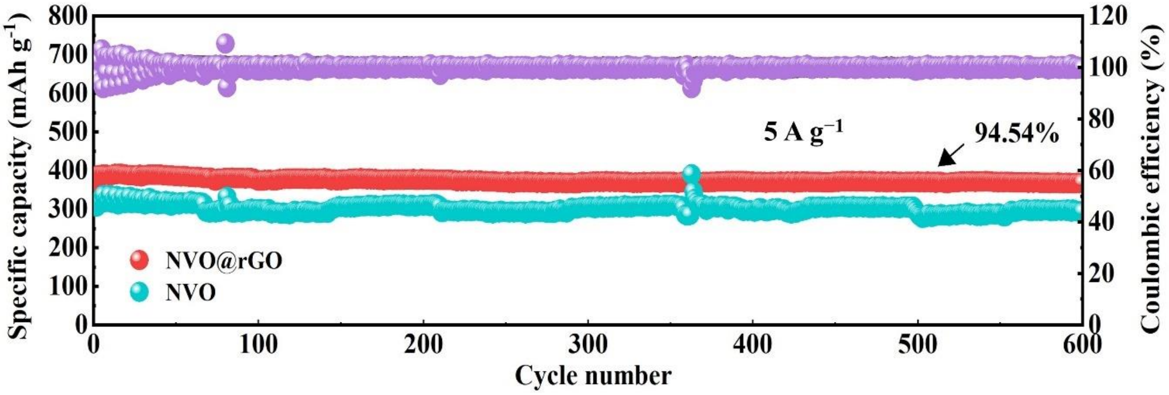

Figure 8. Cycling performance of NVO@rGO, NVO at current density of 5 A g^{-1}.

Long-term cycling performance, illustrated in Figure 8, further highlights the durability of NVO@rGO. Tested at a high current density of 5 A g^{-1}, NVO@rGO demonstrated an initial specific capacity of 388.2 mAh g^{-1} and maintained a retention rate of 94.54% after 600 cycles. In contrast, NVO showed a significantly lower capacity retention under the same conditions. This superior performance of NVO@rGO is indicative of its potential in applications requiring high power outputs and long-term reliability.

To further elucidate the underlying electrochemical reaction mechanisms, CV curves were examined at various scan rates across a potential window of 0.2 to 1.6 V. Figure 9 illustrates the CV profiles for NVO@rGO and NVO, which exhibit similar morphologies, suggesting that analogous electrochemical processes occur within both materials. Notably, as the scan rate increases, both the oxidation and reduction peaks demonstrate shifts of varying magnitudes, a behavior indicative of electrochemical polarization.

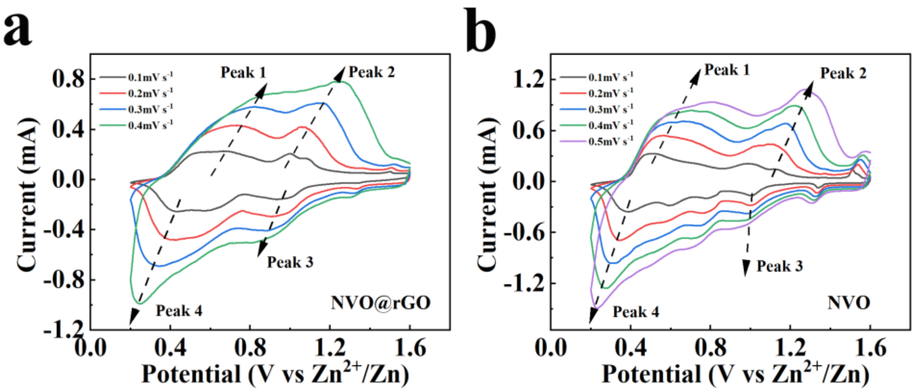

Figure 9. CV curves of (**a**) NVO@rGO and (**b**) NVO at various scan rates.

In these CV analyses, the relationship between the peak current (i) and the scan rate (v) is described by the following equations:

$$i = av^b \quad (1)$$

$$\log(i) = \log(a) + b\log(v) \quad (2)$$

where a and b are constants determined empirically. The coefficient b is particularly informative, indicating the degree to which the electrochemical reactions are governed by diffusion or capacitive processes. Generally, b values that are close to 0.5 suggest a reaction mechanism dominated by diffusion, whereas values approaching 1 imply predominant capacitive control.

The calculated b values, as presented in Figure 10a,b, for the four distinct peaks of NVO@rGO are 0.81, 0.97, 0.84, and 0.96, and for NVO are 0.73, 1, 0.86, and 0.78, respectively. These values, all within the range of 0.5 to 1, confirm that ion transport within these materials is influenced by both diffusion and surface capacitive effects. However, the prevalence of values nearing 1 highlights that capacitive contributions play a significant role in defining their overall capacitance behavior.

The capacitive contributions of NVO@rGO and NVO were quantitatively assessed using the following equation:

$$i = k_1v + k_2v^{1/2} \quad (3)$$

where k_1v denotes the pseudocapacitive contribution, and $k_2v^{1/2}$ reflects the diffusion contribution. This formulation facilitated the calculation of the pseudocapacitive contributions at a scan rate of 0.1 mV s^{-1}. According to the results presented in Figure 11a,b, the pseudocapacitive contribution for NVO@rGO was determined to be 90.78%, compared to 82.48% for NVO. The enhanced pseudocapacitive performance of NVO@rGO can be attributed to the increased surface area resulting from the integration of rGO. This modification promotes more effective surface charge transport, thereby increasing the overall charge transport efficiency within the composite material.

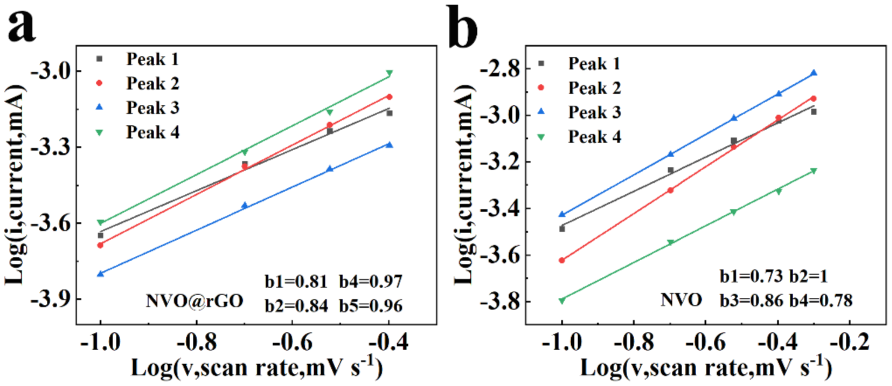

Figure 10. b-value curves of (**a**) NVO@rGO and (**b**) NVO.

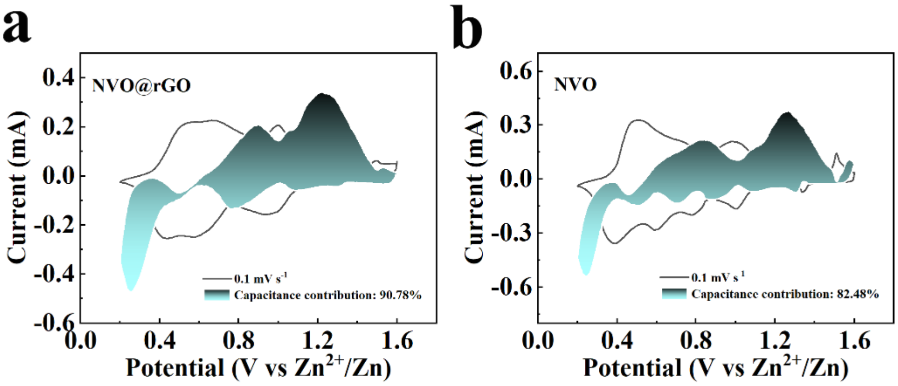

Figure 11. Pseudocapacitance contribution of NVO@rGO and NVO at 0.1 mV s^{-1} scan rate.

Electron paramagnetic resonance (EPR) testing, as depicted in Figure 12a, revealed the presence of oxygen vacancies within the NVO@rGO composite. These defects are crucial as they often act as active sites for electrochemical reactions and can significantly influence the electronic properties and reactivity of the material.

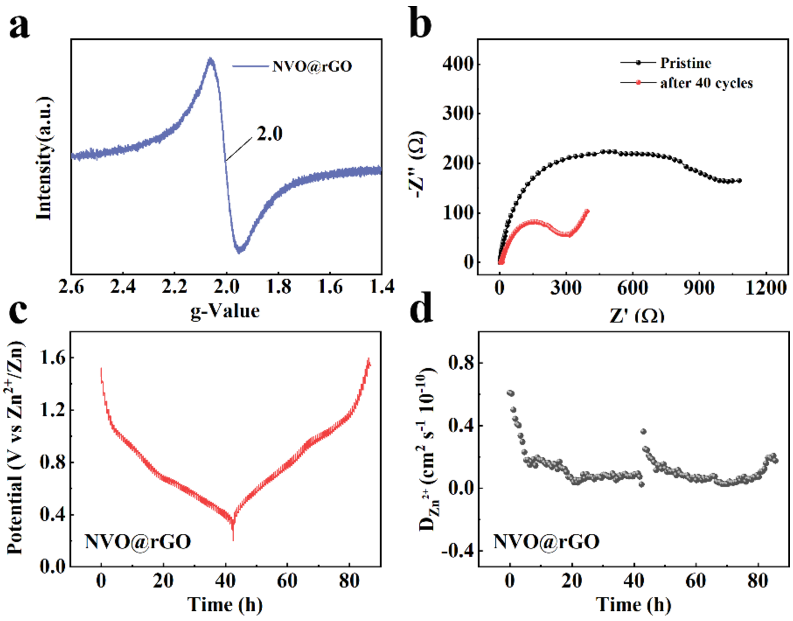

Figure 12. (**a**) EPR profiles, (**b**) EIS profiles and (**c**,**d**) GITT profiles of NVO@rGO.

Further investigation into the electrochemical properties of NVO@rGO was conducted using Electrochemical Impedance Spectroscopy (EIS). EIS analysis was performed to evaluate the charge transfer resistance and the ionic diffusion resistance before and after cycling. The Nyquist plots typically exhibit a semicircular region at high frequencies, corresponding to the charge transfer resistance, and a linear region at low frequencies, indicative of the ionic diffusion resistance. The EIS measurements, conducted over a frequency range from 0.01 Hz to 105 Hz across various cycle numbers, are presented in Figure 12b. Notably, the impedance after 40 cycles is lower than that before cycling, suggesting an enhancement in electrochemical reactivity and conductivity of the composite due to electrochemical activation and possible restructuring of the electrode material during cycling.

Additionally, the Galvanostatic Intermittent Titration Technique (GITT) was employed to determine the diffusion coefficient of Zn^{2+} ions within the material. Conducted at a current density of 0.1 A g^{-1} with a relaxation period of 30 minutes and data logging every 10 seconds, the findings (shown in Figure 12c,d) reveal a Zn^{2+} diffusion coefficient of approximately 10^{-11} cm^2 s^{-1}. This value indicates the mobility of Zn^{2+} ions within the NVO@rGO matrix, which is crucial for assessing the efficiency of ion transport.

2.4. Storage Mechanism of Zn^{2+}

To further investigate the zinc storage mechanism within the NVO@rGO system during electrochemical reactions, analyses were carried out using ex situ XRD and ex situ X-ray photoelectron spectroscopy (XPS). A button cell employing 3 M $Zn(CF_3SO_3)_2$ as the electrolyte was assembled and subjected to ten cycles of charging and discharging. Subsequently, the electrode was extracted, washed with distilled water, and dried prior to XRD examination. The results, presented in Figure 13, show characteristic peaks at 7.44°, 25.06°, 30.32°, 45.84°, and 48.6°. These peaks correspond to the standard diffraction angles for $NH_4V_4O_{10}$, aligning with the (001), (110), (–311), (–205), and (020) crystallographic planes, respectively. The persistence of these peaks throughout the cycling process suggests that the incorporation of reduced graphene oxide (rGO) does not modify the fundamental reaction dynamics within the battery. Notably, the emergence and dissolution of new phases were observed across the entire charging and discharging cycles, indicating dynamic changes in the electrode structure.

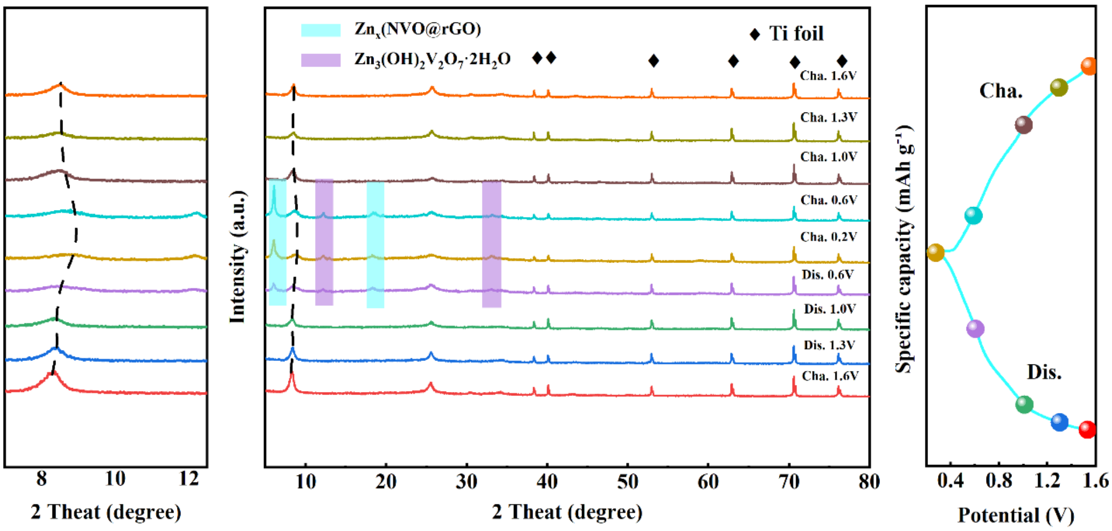

Figure 13. Ex-situ XRD patterns of NVO@rGO at different charge states during the 10th cycle.

In Figure 13, the left portion presents an enlarged view of the (001) crystallographic plane of NVO@rGO. Notably, the peak corresponding to the (001) plane shifts toward higher diffraction angles as the electrode transitions from a charged state at 1.6 V to a discharged state at 0.2 V. This shift indicates a reduction in interlayer spacing, which is attributed to the electrostatic interactions between Zn^{2+} ions and the bilayer structure. When the electrode is returned to the fully charged state at 1.6 V, the peak relocates to its original position, affirming the structural integrity of the NVO@rGO electrode. This resilience is ascribed to the mechanical support and enhanced electrical conductivity provided by graphene within the composite.

Additionally, the XRD data reveal the appearance and subsequent disappearance of two distinct sets of diffraction peaks during the discharge to 0.6 V and recharge to the same voltage. The first set of peaks, located at 5.98° and 18.32°, is associated with the intercalation and deintercalation of Zn^{2+} ions within the NVO@rGO electrode matrix. These peaks disappear as the Zn^{2+} ions are extracted at 0.6 V. A second set of peaks, observed at 12.08° and 33.2°, corresponds to the formation of a new phase, $Zn_3(OH)_2V_2O_7{\cdot}2H_2O$. This phase is a recognized intermediate in the electrochemical processes of vanadium-based AZIBs [36,37], underscoring the dynamic nature of the phase transformations occurring within these cells.

To confirm the presence of the specified compound, SEM analyses were performed on electrodes in their initial state, after discharge to 0.2 V, and following recharge to 1.6 V (Figures 14a–c). The SEM image of the electrode in its initial state revealed no extraneous materials. However, upon discharge to 0.2 V, micrometer-scale flake-like structures emerged on the surface of the active material, consistent with the morphology of $Zn_3(OH)_2V_2O_7{\cdot}2H_2O$ as described in existing literature [38]. These structures subsequently dissipated upon recharging to 1.6 V, aligning with changes observed in ex-situ XRD analyses and demonstrating the reversible intercalation and deintercalation of Zn^{2+} ions throughout the cycling process. To further ascertain the identity of the intermediate phase, the battery was discharged to 0.2 V and subjected to EDS mapping of the micrometer-scale flakes present on the electrode (Figure 14d). The EDS results indicated a uniform distribution of Zn, V, and O within these structures, confirming their composition as $Zn_3(OH)_2V_2O_7{\cdot}2H_2O$.

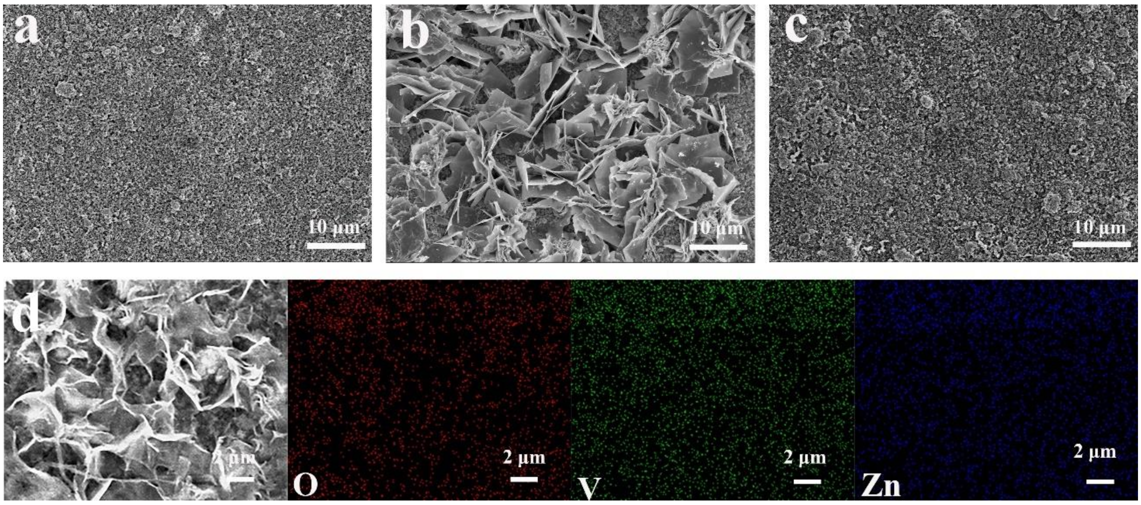

Figure 14. (**a**–**c**) SEM patterns of NVO@rGO under different discharge states; (**d**) Elemental mapping patterns of NVO@rGO under discharge to 0.2 V.

Concurrently, XPS analyses were performed on electrodes in various states: pristine, after discharging to 0.2 V, and after recharging to 1.6 V (Figure 15), to elucidate the chemical state transformations of the cathode material during the electrochemical process. Initially, four prominent peaks were detected: V $2p_{1/2}$ and V $2p_{3/2}$ at 516.39 eV and 523.90 eV respectively, characteristic of V^{4+}, and V $2p_{1/2}$ and V $2p_{3/2}$ at 517.72 eV and 525.26 eV respectively, indicative of V^{5+}. Upon discharging to 0.2 V, an increase in the intensity of V^{4+} peaks was observed, signaling a reduction state favorability. Further, during the discharge to 0.2 V, the vanadium-based cathode material underwent dissolution in the aqueous solution, resulting in the formation of the byproduct $Zn_3(OH)_2V_2O_7{\cdot}2H_2O$ [39]. Subsequent recharging to 1.6 V led to the predominance of V^{5+} over V^{4+}, reverting to the initial electrochemical state and demonstrating the structural reversibility of the cathode material.

In addition, the zinc states were monitored across different levels of discharge. Initially, no peaks corresponding to Zn^{2+} were discernible. Nevertheless, upon discharging to 0.2 V, peaks at 1022.7 eV and 1045.56 eV corresponding to Zn $2p_{1/2}$ and Zn $2p_{3/2}$ manifested, suggestive of Zn^{2+} intercalation. Notably, a residual absorption peak for zinc persisted upon recharging to 1.6 V. This occurrence is a typical reaction artifact, arising from incomplete extraction of Zn^{2+}, thereby resulting in the formation of residual, or "dead" zinc.

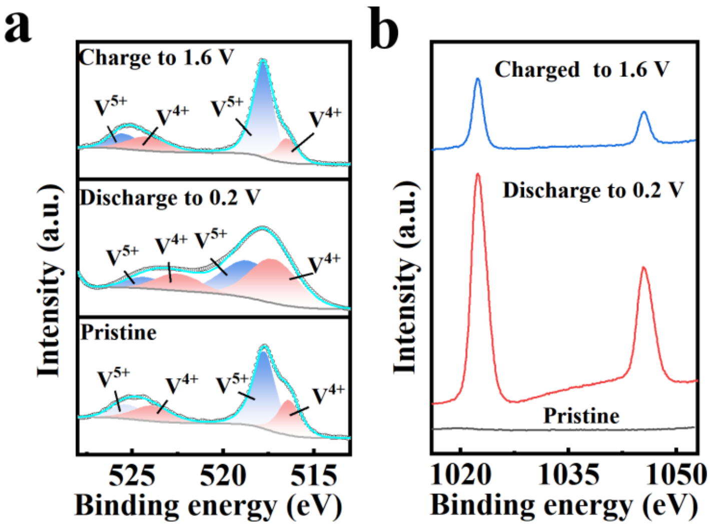

Figure 15. XPS patterns of (**a**) V 2p and (**b**) Zn 2p in the initial state, charging at 1.6 V and discharging at 0.2 V.

3. Materials and Methods

3.1. Calculation Method

The DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [40]. The exchange-correlation interactions were described by the Perdew–Burke–Ernzerhof (PBE) functional [41]. Our computational strategy incorporated a plane-wave basis set, with a chosen energy cutoff of 400 eV, in conjunction with the Projector Augmented Wave (PAW) method [42,43]. We set the convergence thresholds for the self-consistent field iterations at 1×10^{-5} eV, and for the force convergence at 0.01 eV $Å^{-1}$. The Brillouin zone was sampled using a Γ-centered k-point mesh of 2 × 4 × 1 for both the relaxation of the geometric structures and the total energy calculations.

3.2. Preparation of Material

The synthesis of NVO and NVO@rGO was accomplished through a one-step hydrothermal method. Initially, NVO was synthesized by dissolving 8 mmol of ammonium metavanadate in 60 mL of deionized water, which was heated to 60°C until complete dissolution occurred. The solution was then allowed to cool to room temperature. In parallel, 8 mmol of oxalic acid was dissolved in 10 mL of deionized water and was slowly added to the ammonium metavanadate solution with continuous stirring. After vigorous stirring at room temperature for 0.5 hours, the combined solution was transferred to a 100 mL Teflon-lined autoclave and subjected to hydrothermal treatment at 180°C for 24 hours. Upon natural cooling to room temperature, the resultant dark green product was isolated in a centrifuge tube and washed multiple times with alternating cycles of deionized water and anhydrous ethanol, followed by centrifugation. The final product was then freeze-dried for 12 hours to yield NVO.

Subsequently, NVO@rGO was synthesized by first weighing 50 mg of graphene oxide and dispersing it in 50 mL of distilled water, followed by sonication at a frequency of 45 kHz for 0.5 hours. Then, 0.9359 g of NH_4VO_3 was added to this dispersion and dissolved at 60°C, after which the solution was allowed to cool to room temperature. Separately, 1.386 g of $H_2C_2O_4{\cdot}2H_2O$ was dissolved in 10 mL of distilled water. Once dissolved, it was slowly added to the graphene oxide solution containing NH_4VO_3 under vigorous stirring for 0.5 hours. This mixture was then transferred to a 100 mL Teflon-lined autoclave and subjected to a hydrothermal reaction at 180°C for 24 hours. After cooling to room temperature, the resultant black product was processed in the same manner as NVO, involving multiple washes, centrifugation, and freeze-drying, to yield the final product, designated as NVO@rGO.

3.3. Electrode Fabrication

The electrode composition comprising the active material, polyvinylidene fluoride (PVDF) as a binder, and acetylene black as a conductive agent, was added in a 6:3:1 ratio into a mortar. The mixture was ground extensively to ensure uniform blending and achieve a fine, smooth powder. Subsequently, N-methyl-2-pyrrolidone (NMP) was added dropwise, and the mixture was further milled until the resulting paste displayed a shiny surface. Titanium foil was employed as the current collector, onto which the paste was evenly spread. The coated foils were then dried in a vacuum oven at 110 °C for 12 hours. After cooling to room temperature, the electrodes were punched into circular disks of 1 cm diameter, with an active material load of approximately 1.3 mg cm^{-2}.

3.4. Structure and Morphology Characterization

The structural properties of all materials synthesized during the electrochemical process were characterized using XRD with Cu Kα radiation (Smart Lab SE, Tokyo, Japan). Morphological and crystalline features of these materials were systematically investigated using SEM (Hitachi SU8010, Tokyo, Japan) and TEM (FEI Talos F200X, Waltham, MA, USA). The elemental distribution within the samples was analyzed using SEM equipped with EDS. Additionally, XPS (Thermo ESCALAB 250Xi, Waltham, MA, USA) was employed to determine the elemental composition and to monitor changes in the valence states in both powder samples and electrode slices. Furthermore, FTIR (VERTEX 70, Saarbrücken, Germany) was utilized to elucidate the functional groups within the materials, facilitating comprehensive comparative analyses.

3.5. Electrochemical Measurements

The electrochemical properties of the synthesized materials were extensively assessed through the assembly and evaluation of CR2032-type button cells, designated as the prototype cells for this study. During the assembly phase, zinc foil was employed as the anode, whereas titanium foil served as the current collector. A glass fiber material was utilized as the separator. The chosen electrolyte was a 3 M solution of zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$). The entire assembly process was conducted under standard atmospheric conditions and concluded with the cells being hermetically sealed using a specialized sealing apparatus.

CV and EIS tests were conducted using a CHI 760E electrochemical workstation. For the CV measurements, the voltage was applied within a range of 0.2 to 1.6 V, with scan rates adjusted between 0.1 to 0.5 mV s^{-1}. EIS measurements spanned a frequency range from 0.01 Hz to 105 Hz. Furthermore, evaluations of specific capacity, GCD curves, and GITT were performed using the Battery Test System CT2001A, manufactured by Wuhan LAND Electric Co.

4. Conclusions

This study presents a significant advancement in the development of AZIBs through the integration of a novel cathode material, NVO, with rGO. The introduction of rGO to the NVO structure, as hypothesized and supported by DFT calculations, effectively increases the interlayer spacing and reduces charge transfer interactions. This modification facilitates a more efficient diffusion of Zn^{2+} ions, addressing a crucial challenge in the performance of vanadium-based cathode materials. Experimental results from hydrothermal synthesis have validated our theoretical predictions, demonstrating a substantial increase in interlayer spacing. The electrochemical tests further highlight the remarkable durability of the NVO-rGO composite, which retains 94.54% of its initial specific capacity of 506.9 mAh g^{-1} after 600 cycles at a high current density of 5 A g^{-1}. This performance not only surpasses that of pristine NVO but also exceeds the majority of existing vanadium oxide cathode materials in terms of cyclic stability and capacity retention.

These findings underscore the potential of NVO-rGO composites in enhancing the practical applicability of AZIBs, suggesting a pathway to more sustainable, cost-effective, and safer battery technologies. The integration of theoretical insights and experimental validation in this research contributes to the field of energy storage, supporting the transition towards renewable energy sources by improving the efficiency and reliability of energy storage solutions.

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References

1. Jia, X.; Liu, C.; Neale, Z.G.; Yang, J.; Cao, G. Active materials for aqueous zinc ion batteries: synthesis, crystal structure, morphology, and electrochemistry. *Chem. Rev.* **2020**, *120*, 7795–7866.
2. Wan, F.; Niu, Z. Design strategies for vanadium-based aqueous zinc-ion batteries. *Angew. Chem. Int. Edit.* **2019**, *131*, 16508–16517.
3. Chen, S.P.; Lv, D.; Chen, J.; Zhang, Y.H.; Shi, F.N. Review on defects and modification methods of $LiFePO_4$ cathode material for lithium-ion batteries. *Energy Fuels* **2022**, *36*, 1232–1251.
4. Jin, Y.; Zhang, T.; Zhang, M. Advances in intelligent regeneration of cathode materials for sustainable lithium-ion batteries. *Adv. Energy Mater.* **2022**, *12*, 2201526.
5. Zhang, Y.; Xu, J.; Liu, C.; Cheng, H.; Cai X.; Jia, D.; Lin, H. Ion-exchange-induced high-performance of inverse spinel Mg_2VO_4 for aqueous zinc-ion batteries. *J. Power Sources* **2022**, *549*, 232075.
6. Yimtrakarn, T.; Liao, Y.-C.; MV, A.S.; Chen, J.-L.; Chuang, Y.-C.; Lerkkasemsan, N.; Kaveevivitchai, W. Mn-Fe prussian blue analogue as low-cost robust cathode for non-aqueous Zn-ion batteries. *Mater. Today Commun.* **2023**, *34*, 105231.
7. Wu, B.; Zhang, G.; Yan, M.; Xiong, T.; He, P.; He, L.; Xu, X.; Mai, L. Graphene scroll-coated α-MnO_2 nanowires as high-performance cathode materials for aqueous Zn-ion battery. *Small* **2018**, *14*, 1703850.
8. Wang, J.; Liu, Z.; Wang, H.; Cui, F.; Zhu, G. Integrated pyrazine-based porous aromatic frameworks/carbon nanotube composite as cathode materials for aqueous zinc ion batteries. *Chem. Eng. J.* **2022**, *450*, 138051.
9. Guo, C.; Yi, S.; Si, R.; Xi, B.; An, X.; Liu, J.; Li, J.; Xiong, S. Advances on defect engineering of vanadium-based compounds for high-energy aqueous zinc-ion batteries. *Adv. Energy Mater.* **2022**, *12*, 2202039.
10. Ding, Y.; Zhang, L.; Wang, X.; Han, L.; Zhang, W.; Guo, C. Vanadium-based cathodes for aqueous zinc ion batteries: structure, mechanism and prospects. *Chin. Chem. Lett.* **2023**, *34*, 107399.
11. Zhang, N.; Wang, J.-C.; Guo, Y.-F.; Wang, P.-F.; Zhu, Y.-R.; Yi, T.-F. Insights on rational design and energy storage mechanism of Mn-based cathode materials towards high performance aqueous zinc-ion batteries. *Coord. Chem. Rev.* **2023**, *479*, 215009.
12. Chen, D.; Lu, M.; Cai, D.; Yang, H.; Han, W. Recent advances in energy storage mechanism of aqueous zinc-ion batteries. *J. Energy Chem.* **2021**, *54*, 712–726.
13. 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*, 9244–9272.
14. Chen, D.; Lu, M.; Wang, B.; Cheng, H.; Yang, H.; Cai, D.; Han, W.; Fan, H.J. High-mass loading $V_3O_7 \cdot H_2O$ nanoarray for Zn-ion battery: New synthesis and two-stage ion intercalation chemistry. *Nano Energy* **2021**, *83*, 105835.
15. Zhang, N.; Jia, M.; Dong, Y.; Wang, Y.; Xu, J.; Liu, Y.; Jiao, L.; Cheng, F. Hydrated layered vanadium oxide as a highly reversible cathode for rechargeable aqueous zinc batteries. *Adv. Funct. Mater.* **2019**, *29*, 1807331.
16. Zampardi, G.; Mantia, F.L. Prussian blue analogues as aqueous Zn-ion batteries electrodes: Current challenges and future perspectives. *Curr. Opin. Electrochem.* **2020**, *21*, 84–92.
17. Zhou, T.; Zhu, L.; Xie, L.; Han, Q.; Yang, X.; Chen, L.; Wang, G.; Cao, X. Cathode materials for aqueous zinc-ion batteries: A mini review. *J. Colloid. Interf. Sci.* **2022**, *605*, 828–850.
18. Zhou, J.; Shan, L.; Wu, Z.; Guo, X.; Fang, G.; Liang, S. Investigation of V_2O_5 as a low-cost rechargeable aqueous zinc ion battery cathode. *Chem. Commun.* **2018**, *54*, 4457–4460.

19. Chen, L.; Yue, H.; Zhang, Z.; Ma, Y.; Wang Y.; Xu, M.; Huang, Y.; Yuan, G. Pre-removing partial ammonium ions from the interlayer of ammonium vanadate with acid treating for quasi-solid-state flexible zinc ion batteries. *Chem. Eng. J.* **2023**, *455*, 140679.
20. Yin, B.; Zhang, S.; Ke, K.; Lee, W.S.V.; Wang, Z. Effects of small molecule interlayer engineering in vanadium oxide for zinc ion battery. *ChemistrySelect* **2020**, *5*, 8951–8958.
21. Tang, B.; Zhou, J.; Fang, G.; Liu, F.; Zhu, C.; Wang, C.; Pan, A.; Liang, S. Engineering the interplanar spacing of ammonium vanadates as a high-performance aqueous zinc-ion battery cathode. *J. Mater. Chem. A* **2019**, *7*, 940–945.
22. He, P.; Quan, Y.; Xu, X.; Yan, M.; Yang, W.; An, Q.; He, L.; Mai, L. High-performance aqueous zinc-ion battery based on layered $H_2V_3O_8$ nanowire cathode. *Small* **2017**, *13*, 1702551.
23. Li, K.; Liu, Y.; Wu, X. Ammonium vanadate electrode materials with stable layered structures for rechargeable zinc ion batteries. *CrystEngComm* **2022**, *24*, 5421–5427.
24. Xu, L.; Zhang, Y.; Zheng, J.; Jiang, H.; Hu, T.; Meng, C. Ammonium ion intercalated hydrated vanadium pentoxide for advanced aqueous rechargeable Zn-ion batteries. *Mater. Today Energy* **2020**, *18*, 100509.
25. Xu, J.; Zhang, Y.; Liu, C.; Cheng, H.; Cai, X.; Jia, D.; Lin, H. Al^{3+} introduction hydrated vanadium oxide induced high performance for aqueous zinc-ion batteries. *Small* **2022**, *18*, 2204180.
26. Tamilselvan, M.; Sreekanth, T.V.M.; Yoo, K.; Kim, J. Wide interlayer spacing ammonium vanadate $(NH_4)_{0.37}V_2O_5{\cdot}0.15(H_2O)$ cathode for rechargeable aqueous zinc-ion batteries. *J. Ind. Eng. Chem.* **2021**, *93*, 176–185.
27. He, D.; Sun, T.; Wang, Q.; Ma, T.; Zheng, S.; Tao, Z.; Jiang, J. Multi-functional potassium ion assists ammonium vanadium oxide cathode for high-performance aqueous zinc-ion batteries. *Batteries* **2022**, *8*, 84.
28. Qi, Y.; Huang, J.; Yan, L.; Cao, Y.; Xu, J.; Bin, D.; Liao, M.; Xia, Y. Towards high-performance aqueous zinc-ion battery via cesium ion intercalated vanadium oxide nanorods. *Chem. Eng. J.* **2022**, *442*, 136349.
29. Xu, L.; Zhang, Y.; Zheng, J.; Jiang, H.; Hu, T.; Meng, C. Ammonium ion intercalated hydrated vanadium pentoxide for advanced aqueous rechargeable Zn-ion batteries. *Mater. Today Energy* **2020**, *18*, 100509.
30. Wang, G.; Kuang, Q.; Jiang, P.; Fan, Q.; Dong, Y.; Zhao, Y. Integrating molybdenum into zinc vanadate enables $Zn_3V_2MoO_8$ as a high-capacity Zn-supplied cathode for Zn-metal free aqueous batteries. *Nanoscale* **2023**, *15*, 6722–6731.
31. Fan, L.; Li, Z. Highly stable cathode materials for aqueous Zn ion batteries: synergistic effect of pre-inserted bimetallic ions in vanadium oxide layer. *J. Alloy. Compd.* **2022**, *910*, 164872.
32. Cui, F.; Hu, F.; Yu, X.; Guan, C.; Song, G.; Zhu, K. In-situ tuning the NH_4^+ extraction in $(NH_4)_2V_4O_9$ nanosheets towards high performance aqueous zinc ion batteries. *J. Power Sources* **2021**, *492*, 229629.
33. Wang, W.; Liu, D.; Jiang, Y.; Zhang, D.; Shen, X.; Li, S.; Liang, J.; Xu, H. Mechanism enhancement of V_3O_7/V_6O_{13} heterostructures to achieve high-performance aqueous Zn-Ion batteries. *Chem. Eng. J.* **2023**, *463*, 142309.
34. Li, S.; Xu, X.; Wang, K.; Chen, W.; Lu, X.; Song, Z.; Hwang, J.Y.; Kim, J.; Bai, Y.; Liu, Y.; Xiong, S. Textured $Na_2V_6O_{16}{\cdot}3H_2O$ cathode tuned via crystal engineering endows aqueous Zn-ion batteries with high rate capability and adequate lifespan. *ACS Energy Lett.* **2022**, *7*, 3770–3779.
35. Wu, J.; Yang, Z.; Chen, H. Oxygen-deficient $HNaV_6O_{16}{\cdot}4H_2O$@reduced graphene oxide as a cathode for aqueous rechargeable zinc-ion batteries. *Ind. Eng. Chem. Res.* **2022**, *61*, 10640–10649.
36. Wu, Q.; Li, X.; Fan, H.; Cao, J.; Liu, X.; Wei, M.; Yang, L. Synergistic interlayer and structure engineering construction of layered hydrated vanadates/graphene for stable aqueous zinc-ion batteries. *J. Alloy. Compd.* **2023**, *941*, 168936.
37. Yi, T.F.; Qiu, L.; Qu, J.P.; Liu, H.; Zhang, J.H.; Zhu, Y.R. Towards high-performance cathodes: design and energy storage mechanism of vanadium oxides-based materials for aqueous Zn-ion batteries. *Coordin. Chem. Rev.* **2021**, *446*, 214124.
38. Ren, H.Z.; Zhang, J.; Wang, B.; Luo, H.; Jin, F.; Zhang, T.R.; Ding, A.; Cong, B.W.; Wang, D.L. A V_2O_3@N–C cathode material for aqueous zinc-ion batteries with boosted zinc-ion storage performance. *Rare Metals* **2022**, *41*, 1605–1615.
39. Xing, Z.; Xu, G.; Xie, X.; Chen, M.; Lu, B.; Zhou, J.; Liang, S. Highly reversible zinc-ion battery enabled by suppressing vanadium dissolution through inorganic Zn^{2+} conductor electrolyte. *Nano Energy* **2021**, *90*, 106621.
40. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169–11186.
41. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
42. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758–1775.
43. Blöchl, P.E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979.

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