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Introduction

The rechargeable batteries are an important cornerstone of world economic development and human survival. Due to the high energy/power density densities, superb service life as well as portability, the rechargeable batteries are widely used in new energy vehicles, smart grids, flexible electronic equipment, distributed energy storage systems, military equipment, and urban rail transit.1, 2 As far as we know, the rechargeable batteries use external electrical energy to regenerate the internal active material, and can be recharged through reversible chemical reactions. Notwithstanding, there is usually no power supply system in remote areas and harsh environments, which means that rechargeable batteries cannot be used secondly and cannot realize their actual value. To break through this bottleneck, scientists invented and created a self-charging power system, which consists of batteries and all sorts of energy harvesting technologies, for instance, photovoltaic devices, piezoelectric nanogenerators, triboelectric nanogenerators, and thermoelectrics. Regrettably, the above-mentioned integrated systems completely depend on energy resources, which cannot be obtained anytime and anywhere. Compared with the conventional two-electrode battery, the structure of these integrated systems is obviously much more complicated, which must be equipped with many additional components at the same time. Consequently, the advanced self-charging power supply system must have a simple structure and function well no matter when and where.

Among the many energy sources, chemical energy is a kind of energy source stored in chemical molecules, which can be obtained anytime and anywhere, and transformed into electrical energy via oxidation-reduction reactions. As a rich air resource, the chemical energy of oxygen has attracted widespread attention in energy conversion and storage devices, and the best known of these are metal-air batteries. Moreover, metal-air batteries could also be extended to integrated appliances, in which the metal-air batteries can provide energy for energy storage devices. Unfortunately, the energy loss of the energy storage device will be unable to reimburse by the metal-air batteries without limitation. When the energy of both parts is exhausted, it must be recharged.
through an external power source to recover. Quite evidently, the above-mentioned integrated devices cannot be directly charged by the continuous oxidation-reduction reaction of oxygen on the cathodes of the batteries. Lately, profiting from a good many advantages, such as high voltage, large theoretical capacity, environmental friendliness, and source abundance, zinc manganite (ZnMn$_2$O$_4$) is considered as a rising star of positive materials for aqueous zinc ion batteries.$^{26-30}$ For ZnMn$_2$O$_4$ aqueous zinc ion batteries, the intercalation of zinc ions and the reduction of manganese will take place simultaneously in the discharge process. Furthermore, manganese oxide compounds with low valence state (such as Mn$^{4+}$, Mn$^{3+}$) have good redox kinetics, which should be capable of being oxidized by oxygen. As a consequence, the positive electrode ZnMn$_2$O$_4$ can undergo an oxidation-reduction reaction with oxygen in the air after discharge, which is able to convert chemical energy into electrical energy. Therefore, chemical self-charging aqueous zinc ion batteries (SCSAZIBs) can realize energy conversion and storage at the same time. Unfortunately, the ZnMn$_2$O$_4$ suffers from intrinsically weak conductivity and large volume change during the charging and discharging, leading to rapid capacity decay and poor rate performance that limit its further development.

In this work, we design a novel nitrogen doped ZnMn$_2$O$_4$ with rich oxygen defects (N-ZnMn$_2$O$_{4-x}$) on three-dimensional vertical graphene (VG) forming N-ZnMn$_{2-x}$@VG core/shell arrays as binder-free cathodes for CSCAZIBs. The specific VG skeleton not only offers an excellent conductive network for N-ZnMn$_2$O$_{4-x}$, and improves reaction kinetics, but also can effectively buffer volume changes during the reaction. Furthermore, the introduced symbiotic nitrogen dopant and oxygen defects can boost the intrinsic electronic conductivity and active sites of ZnMn$_2$O$_4$. The CASCZIBs batteries system has a simple two-electrode structure, and could convert the chemical energy from surrounding into electrical energy via spontaneous redox reaction and store. For that reason, the as-assembled integrated device does not need any outside power, and self-charging could be achieved by putting the N-ZnMn$_{2-x}$@VG electrode in the natural environment. Most important, the CASCZIBs can work well in chemical or/and galvanostatic charging hybrid modes. This work is believed to bring new inspiration to the development of self-powered systems.

**Experimental**

**Synthesis of VG arrays.**

We use a microwave plasma enhanced chemical vapor deposition (MPECVD) system to prepare a uniform VG array on carbon cloth. During the preparation process, the microwave source was set to 2 kW and 2.45 GHz. We first put the carbon cloth in the center of the quartz tube, and then evacuate the quartz tube to 10 mTorr. As the hydrogen flow rate reaches 90 sccm, we increased the temperature of the system to 400 °C. A microwave plasma with 550 W was used to obtain hydrogen plasma, which lasted for 2 h. The flow rate ratio of H$_2$ to CH$_4$ is set to be 3:2. At last, we can gain the end product after it was rinsed with deionized water several times and dry (0.5 mg cm$^{-2}$).

**Synthesis of ZnMn$_2$O$_4$/VG and N-ZnMn$_{2-x}$@VG core/shell arrays.**

We use an electrochemical workstation (CHI 760E) to prepare ZnMn$_2$O$_4$/VG through a facile anodic electrodeposition approach. In the process of sample preparation, we use a traditional three-electrode system, including working electrode (a piece of VG arrays carbon cloth (2 x 3 cm$^2$)), counter electrode (Pt sheet), and reference electrode (Ag/AgCl). zinc nitrate (0.2841 g), manganese nitrate (0.5368434 g), sodium nitrate (0.147 g), and sodium dodecyl sulfate (0.28838 g) were added into deionized water (25 ml), then stir with a magnetic stirrer for half an hour to thoroughly dissolve it. The solution prepared above is used as the electrolyte for the anodic electrodeposition reaction. The sample prepared above was rinsed with deionized water, then heated in air. The specific experimental parameters were as follows: the heating temperature was 300 °C, the heating time was 2 h, and the heating rate was 5 °C min$^{-1}$. When the autoclave was naturally cooled to 25°C, we got the ZnMn$_2$O$_4$ sample (5.6 mg cm$^{-2}$). To prepare N-ZnMn$_{2-x}$/VG core/shell arrays, the obtained ZnMn$_2$O$_4$/VG was further heat treated in NH$_3$ at 500 °C for 4 h, and the N-ZnMn$_{2-x}$/VG core/shell arrays sample is measured to be 5.8 mg cm$^{-2}$.

**Materials characterization.**

We used X-ray diffraction (XRD, Rigaku D-MAX 2200) to probe the crystal structure of the samples. Observations of microscopic features were performed on field-emission scanning electron microscopy ((FESEM, JSM-6330F) and transmission electron microscopy (TEM, FEI Tecnai G2 F30). X-ray photoelectron spectroscopies (XPS) were corrected from ESCALab250 system. We collected the Raman spectra of the samples from the Renishaaraman microscope, which has a laser excitation wavelength of 514 nm. A Bruker EPR spectrometer (A300-10-12) was used to collected electron paramagnetic resonance (EPR) spectra. The synchrotron-based X-ray absorption near-edge structures (XANES) were obtained from beamlines BL10B.

**Electrochemical Measurement.**

The electrochemical behaviors were investigated in CR2032 coin cells using a two-electrode system. The as-prepared ZnMn$_2$O$_4$/VG and N-ZnMn$_{2-x}$/VG samples with a working area of 0.5 cm$^2$ were directly used as the cathode, and zinc plate was used as the anode. In the coin cells, the separator was a commercial glass fiber membrane, and the electrolyte was Zn(CF$_3$SO$_2$)$_2$ solution with a concentration of 4 mol L$^{-1}$. A PARSTAT MC electrochemical workstation was adapted to measure cyclic voltammetry (CV) curves, galvanostatic charge–discharge (GCD) profiles, Mott-Schottky plots, and reaction N-ZnMn$_{2-x}$/VG and O$_2$, the assembled N-ZnMn$_{2-x}$/VG/Zn battery was first discharged to 0.8 V at 0.1 A g$^{-1}$. Afterwards, the positive material (N-ZnMn$_{2-x}$) after the complete discharge was rinsed with ethanol and deionized water.
water three times, respectively. The naturally dried N-ZnMn$_2$O$_4$ electrode was immersed in the electrolyte to cause oxidation-reduction reaction with the oxygen dissolved in the electrolyte. After the reaction, the electrochemical performances of the N-Zn$_{1-x}$Mn$_2$O$_{4+x}$ positive electrode were tested using CR2032 coin cells, which contain a zinc plate negative electrode. In order to allow oxygen in the air to enter the electrolyte of the system during the chemical self-charging, a hole was drilled in the positive cap of the cell in advance. Before starting the chemical self-charging, we sealed the cell with a Kapton membrane. When the redox reaction was needed, the Kapton membrane was torn off to allow oxygen to pass through the hole. The cell would be again with Kapton membrane until the chemical self-charging ends. In addition, the chemical self-charging was executed in an environment with humidity greater than 60% during the entire operation, which can effectively avoid excessive evaporation of water in the electrolyte.

**Results and discussion**

The freestanding N-ZnMn$_2$O$_{4-x}$/VG shell/core arrays were prepared via an electrodeposition (ED) method and subsequent NH$_3$ annealing (NA) process, as schematically shown in Figure 1a. In the first place, the freestanding VG arrays were prepared uniformly on the carbon cloth substrate by an MPECVD method. Then, these ZnMn$_2$O$_4$ nanoparticles were evenly deposited on the VG skeleton by a facile ED method, and formed ZnMn$_2$O$_4$/VG core/shell arrays. Finally, self-supported N-ZnMn$_2$O$_{4-x}$/VG shell/core arrays were got through heating ZnMn$_2$O$_4$/VG under NH$_3$ atmosphere, which was run at 500 °C and lasted 4 h. The morphology variation of these samples at various stages is revealed in SEM images (Figure 1b-d). The thin graphene nanosheets with several nanometers are vertically grown on the carbon cloth substrate with a freestanding arrays structure (Figure 1b). The VG nanosheets are connected to each other and developed into a three-dimensional porous network with an interspace of 50-500 nm, which is an excellent conductive skeleton and conducive to the rapid transmission of ions/electrons. When the ED growth is finished, the ZnMn$_2$O$_4$ nanoparticles are perfectly fused with the VG skeleton (Figure 1c), in which the former is evenly covered on the latter to form a self-supporting core/shell array structure. Evidently, the thickness of the ZnMn$_2$O$_{4-x}$/VG core/shell arrays is much thicker than that of the original VG array. Followed by the NH$_3$ annealing process, the microstructure of the final N-ZnMn$_2$O$_{4-x}$/VG has no obvious change compared with the original sample (Figure 1d). It should be noted that the three-dimensional porous architecture is still well kept throughout the process, which would help the fully contact between electrode and electrolyte, speed up the transmission of electrons/ions, and improve the conductivity. The microstructures and crystalline features of the three samples are further monitored with TEM measurements. It can be seen from Figure 1e that the graphene nanosheet has a...
smooth corrugated texture and a very thin thickness. The distance between graphene interlayer is gauged to be 0.37 nm, and it is in good agreement with the (002) plane of graphitic carbon (inset in Figure 1e). The TEM image of the ZnMn$_2$O$_4$/VG arrays is depicted in Figure 1f, in which the ZnMn$_2$O$_4$ nanoparticles can firmly adhere to the VG framework, and form a core-shell structure. As revealed by the inset of Figure 1f, the ZnMn$_2$O$_4$ shell has an interlayer distance of 0.30 nm, and could be well matched with the (112) plane from the ZnMn$_2$O$_4$ phase (JCPDS No. 24–1133), further attesting the successful formation of the ZnMn$_2$O$_4$ on the VG arrays. After ammonia heat treatment, the N-ZnMn$_2$O$_4$/VG array in Figure 1g still retains the microstructure of ZnMn$_2$O$_4$/VG array, and the corresponding interlayer spacing is calculated to be 0.47 nm (inset of Figure 1g) that belongs to the (101) plane of ZnMn$_2$O$_4$ (JCPDS No. 24–1133). What is more, In the HRTEM image of the N-ZnMn$_2$O$_4$/VG arrays, we can clearly see the zigzag lattice fringes, which indicate that the sample has stacking faults causing by oxygen defects. Additionally, the energy dispersive X-ray (EDS) mapping images confirm that Zn, Mn, O, C, and N elements can be homogeneously distributed on the N-ZnMn$_2$O$_4$/VG core/shell arrays (Figure 1h-l), verifying the successful fabrication of N-ZnMn$_2$O$_4$/VG and uniform deposition on the VG arrays skeleton.

To further explore the crystal structure and phase evolution, XRD and Raman measurements were carried out. The diffraction peaks of the ZnMn$_2$O$_4$/VG and N-ZnMn$_2$O$_4$/VG samples at about 26° in Figure S1 could be associated with the VG skeleton (JCPDS 75-1621). In addition to VG (002) peak, the other diffraction peaks from both samples can correspond well to the spinel ZnMn$_2$O$_4$ (JCPDS No. 24–1133), indicating that they do not contain other impurities. Compared with ZnMn$_2$O$_4$/VG, the diffraction peaks of N-ZnMn$_2$O$_4$/VG are less intense, which is probably due to the decrease in crystallinity. The lower crystallinity added a further effective diffusion channels to electrocatalyst and ions, which would be greatly accelerate the rate of electrochemical reaction.\textsuperscript{31} Figure S2 displays the Raman spectra of the ZnMn$_2$O$_4$/VG and N-ZnMn$_2$O$_4$/VG. The Zn-O bond (321 and 378 cm$^{-1}$) and Mn-O bond (673 cm$^{-1}$) are observed in the ZnMn$_2$O$_4$/VG sample.\textsuperscript{28, 32} and those Raman peaks manifest distinctly red shift with decreased intensities after ammonia heat treatment, probably caused by the introduced oxygen defects and nitrogen doping.\textsuperscript{33, 34} More information about the oxygen defects and nitrogen doping would be supplied by the XPS, XANES, and EPR spectra. As evidenced in Figure S3, the Zn, Mn, O, C and N elements are demonstrated to be present in N-ZnMn$_2$O$_4$/VG, which consistent with the above EDS analysis. In the Mn 2p spectra of ZnMn$_2$O$_4$/VG, the Mn 2p$_3/2$ and Mn 2p$_1/2$ peaks are located at 642.2 and 653.9 eV, respectively (Figure 2a). Noticeably, the two peaks shift negatively to a lower position (about 0.4 eV) for the N-ZnMn$_2$O$_4$/VG. Meanwhile, similar red shifts are also observed in Mn L-edge spectra (0.94 eV, Figure 2b) and Mn 3s spectra (0.44 eV, Figure 54). The clearly red shift in Mn 2p and Mn L-edge, as well as the Mn 3s spectra for N-ZnMn$_2$O$_4$/VG, representing manganese ions are reduced from trivalent to bivalent due to the oxygen defects.\textsuperscript{33, 35} The O 1s spectra of the ZnMn$_2$O$_4$/VG and N-ZnMn$_2$O$_4$/VG are illustrated in Figure 2c. The characteristic peak belonging to the Mn-O bond (529.9 eV) is inspected in both samples. Yet, the N-ZnMn$_2$O$_4$/VG sample has two new strong peaks at 531.2 and 532.8 eV. Specifically, the peak at 531.2 eV is associated with the Mn-OH bond, which may result from oxygen defect sites in the N-ZnMn$_2$O$_4$/VG sample. Meanwhile, the peak at 532.8 eV is relating to the O-H bond, and its strength has been greatly improved after heat treatment, indicating that a lot of surface adsorbed water adheres to the surface of the N-ZnMn$_2$O$_4$/VG. These results prove that the N-ZnMn$_2$O$_4$/VG has more surface active sites and is easier to absorb electrolyte, leading to a smooth electrochemical reaction.\textsuperscript{36} The O K-edge spectrum is a powerful technique in characterizing changes in the electronic valence state, and it is often used to investigate the change between O 1s core state and unoccupied O 2p derived state.

**Figure 2.** Core-level spectra of (a) Mn 2p, (c) O1s, (e) N1s. NEXAFS spectra for (b) Mn L3-edge, (d) O K-edge. (f) EPR spectra of ZnMn$_2$O$_4$/VG and N-ZnMn$_2$O$_4$/VG.
involving the hybridization with the 3d and 4sp bands in metal ions. The peak of N-ZnMnO\textsubscript{4}/VG at 534.5 eV is much broader than that of the original ZnMnO\textsubscript{2}/VG (Figure 2d), and it is probably the oxygen defects in N-ZnMnO\textsubscript{4}/VG that give rise to this phenomenon. Interestingly, no relative displacement is observed in the Zn 2p for the two samples, which reveals that there is no change in the valence state of zinc (Figure S5). As shown in the N 1s spectra in Figure 2e, the N-ZnMnO\textsubscript{4}/VG sample exhibits evident N-Mn bonds compare to the native ZnMnO\textsubscript{2}/VG, which proves that the nitrogen atoms are strongly combined with the manganese atoms, and leading to red shift phenomenon in XPS 2p and L-edge spectra of Mn atoms. Moreover, the Mn K-edge XPS spectra of N-ZnMnO\textsubscript{4}/VG move to low binding energy (Figure S6), suggesting a higher average electron density, which results in the red shift in binding energy and photon energy of Mn element in XPS and XANES measurements. More evidence about the oxygen vacancies can also be found in EPR spectra. The N-ZnMnO\textsubscript{4}/VG shows a much stronger peak at a g value of 1.998 in Figure 2f, indicating Mn\textsuperscript{2+} are generated and oxygen vacancies are formed during the annealing process. Besides, the Mott-Schottky plot of N-ZnMnO\textsubscript{4}/VG in Figure S7 has an absolute value of slope of about 2.06, which is much smaller than that of the ZnMnO\textsubscript{2}/VG electrode (9.26), confirming the oxygen vacancies are successfully introduced into N-ZnMnO\textsubscript{4}/VG and greatly enhanced the carrier density.

The zinc storage performances of N-ZnMnO\textsubscript{4}/VG electrode were explored as positive electrode for zinc ion batteries in 4 M Zn(C\textsubscript{2}S\textsubscript{4})\textsubscript{2} electrolyte. Figure 3a depicts the CV curves of the ZnMnO\textsubscript{2}/VG and N-ZnMnO\textsubscript{4}/VG electrode, which were measured with 0.5 mV s\textsuperscript{-1} in the range of 0.8 to 1.8 V. Note that both ZnMnO\textsubscript{2}/VG and N-ZnMnO\textsubscript{4}/VG exhibit oxidation peaks during the anodic sweeping, and reduction peaks in the cathodic scan. The two well separated reduction peaks are due to the intercalation of H\textsuperscript{+} and Zn\textsuperscript{2+} step by step, and the Mn\textsuperscript{4+} would be reduced to the low valence state during the process. While the two oxidation peaks should be connected with the oxidation of Mn\textsuperscript{3+}/Mn\textsuperscript{4+} back to Mn\textsuperscript{4+} state upon the H\textsuperscript{+} and Zn\textsuperscript{2+} extraction. The current density of the CV curve in N-ZnMnO\textsubscript{4}/VG is obviously larger when measured against the corresponding ZnMnO\textsubscript{2}/VG, proving a superior reactivity and utilization. In addition, the N-ZnMnO\textsubscript{4}/VG electrode displays smaller polarization than that of the ZnMnO\textsubscript{2}/VG counterpart. In addition, the N-ZnMnO\textsubscript{4}/VG electrode displays smaller polarization than that of ZnMnO\textsubscript{2}/VG counterpart, which can be mutually confirmed with the GCD curves in Figure 3b that received at 0.1 A g\textsuperscript{-1}. The first and second discharge platforms are attributed to the intercalation of H\textsuperscript{+} and Zn\textsuperscript{2+}, respectively. Notably, the N-ZnMnO\textsubscript{4}/VG sample has much better charging/discharging platform and charge-discharge capacity, represent smaller polarization and higher power/energy densities that benefit from the abundant oxygen defects, nitrogen doping, and VG skeleton. These GCD curves of both samples in Figure S8 that measured at various current densities could be capable of achieving a similar conclusion as well. Rapid charge-discharge performance is an important index for the application of zinc ion batteries. The N-ZnMnO\textsubscript{4}/VG electrode could deliver capacities of 222, 212.3, 195.6, 173.2, 153.4, and 136.7 mAh g\textsuperscript{-1}, when cycled at 0.1, 0.2, 0.5, 1.0, 2.0, and 3.0 A g\textsuperscript{-1}, respectively (based on N-ZnMnO\textsubscript{4}/VG). Additionally, capacity retention of 61.58% is also achieved while the rate changes from 0.1 to 3.0 A g\textsuperscript{-1}. It was imperative that the capacity of the N-ZnMnO\textsubscript{4}/VG electrode could be restored to 219 mAh g\textsuperscript{-1} when tested with 0.1 A g\textsuperscript{-1} again. Such rate performance surpasses the ZnMnO\textsubscript{2}/VG and other ZnMnO\textsubscript{2}-based electrodes (Table S1).

Besides, the N-ZnMnO\textsubscript{4}/VG electrode manifests a much smaller semicircle and steeper straight line compared with the original ZnMnO\textsubscript{2}/VG electrode (Figure 3d), suggesting superior electron and ion diffusion rate. These results are further substantiated by the GITT measurements in Figure 3e, which may be able to evaluate the zinc ion diffusion coefficient (D\textsubscript{Zn}) in both electrodes. The average D\textsubscript{Zn} of the N-ZnMnO\textsubscript{4}/VG electrode is in the range of 10\textsuperscript{-11} to 10\textsuperscript{-13} cm\textsuperscript{2} s\textsuperscript{-1}, which is superior to ZnMnO\textsubscript{2}/VG electrode, discovering the boosted kinetics for N-ZnMnO\textsubscript{4}/VG electrode after annealing treatment, ensuring favorable rate capability. These b-values in Figure S9 suggest that the zinc ions storage of the two electrodes is controlled by the surface capacitive effect. The N-ZnMnO\textsubscript{4}/VG electrode has a better capacitive contribution in contrast to the primitive ZnMnO\textsubscript{2}/VG, which signifies more advanced surface reactivity in N-ZnMnO\textsubscript{4}/VG, facilitating zinc ion diffusion, high rate enhance, and cyclic stability. As revealed in Figure 3f, the N-ZnMnO\textsubscript{4}/VG electrode has a
great cycle life at 1 A g\(^{-1}\), which delivers a reversible capacity up to 173.2 mAh g\(^{-1}\) (92.6% retention) after 3000th cycles, outperform the value of ZnMn\(_2\)O\(_4\)/VG sample and the recently reported ZnMn\(_2\)O\(_4\)-based cathodes in the Table S1. Plus, the cycle lives were tested at 0.1, 0.5, and 3.0 A g\(^{-1}\) are also presented in Figure S10 for a more in-depth insight into its cycle stability. The Ragone plots in Figure 3g once again prove the good electrochemical performance of the N-ZnMn\(_2\)O\(_4\)/VG/Zn battery. The N-ZnMn\(_2\)O\(_4\)/VG//Zn battery exhibits a peak specific energy density reach 278 Wh kg\(^{-1}\), outperforming those of Ni\(_{x}\)S\(_2\)//AC battery (18.63 W h kg\(^{-1}\)),\(^{44}\) Al//graphite battery (40 W h kg\(^{-1}\)),\(^{45}\) LiMn\(_2\)O\(_4//MoO\(_3\) battery (45 W h kg\(^{-1}\)),\(^{46}\) Ni/|Bi battery (85.8 W h kg\(^{-1}\)),\(^{47}\) Ni/|Fe battery (100.7 W h kg\(^{-1}\)),\(^{48}\) VS\(_2\)/Zn battery (123 W h kg\(^{-1}\)),\(^{49}\) MoS\(_2//\)Zn battery (148.2 W h kg\(^{-1}\)) looking at NNA@Zn (148.5 W h kg\(^{-1}\)),\(^{50}\) H\(_2\)V\(_2\)O\(_7//\)VG//Zn battery (168 W h kg\(^{-1}\)),\(^{51}\) \(\beta\)-Ni\(_{2}\)V\(_2\)O\(_7//\)VG//Zn battery (237.2 W h kg\(^{-1}\)) looking at NNA@Zn (148.5 W h kg\(^{-1}\)),\(^{52}\) \(\beta\)-Ni\(_{2}\)V\(_2\)O\(_7//\)VG//Zn battery (237.2 W h kg\(^{-1}\)) looking at NNA@Zn (148.5 W h kg\(^{-1}\)),\(^{53}\) and \(\beta\)-Ni\(_{2}\)V\(_2\)O\(_7//\)VG//Zn battery (243.3 W h kg\(^{-1}\)).\(^{54}\) More strikingly, the top power density as high as 3.62 kW kg\(^{-1}\) stayed ahead of the others reported aqueous batteries devices.\(^{27, 55-59}\)

For illustration purposes, two N-ZnMn\(_2\)O\(_4//\)VG/Zn batteries are connected up at 1 A g\(^{-1}\) with series or parallel mode, which can achieve a twofold voltage window or capacity (Figure 3h). It shows that we can change the number of devices and connection mode to attain the goal of different voltage windows and capacities. Additionally, Figure 5i proves that N-ZnMn\(_2\)O\(_4//\)VG//Zn batteries could power a digital watch and light emitting diode (LED) lights, revealing a great application potential. The superior high rate properties and long cycle life of the N-ZnMn\(_2\)O\(_4//\)VG electrode are because of the favorable factors as below: (1) Oxygen vacancies and doped nitrogen may be able to increase the active sites and boost conductivity of the N-ZnMn\(_2\)O\(_4//\)VG//Zn batteries. (2) The N-ZnMn\(_2\)O\(_4//\)VG//Zn batteries are uniformly deposited on the VG skeleton with good conductivity, coupled with the three-dimensional porous network, which not only offers a large surface area and more active sites, but also improves the electron/ion transporting efficiency and diminishes polarization. (3) The three-dimensional porous skeleton and the intimate interfacial adhesion between N-ZnMn\(_2\)O\(_4//\)VG//Zn batteries. (4) The electrode without any binders and additives can make the electron and ion diffusion faster and smoother, which will greatly give impetus to the surface reaction and kinetic process. All these strong points dedicate the exceptional electrochemical properties for N-ZnMn\(_2\)O\(_4//\)VG//Zn batteries. The redox potential difference (ΔE) between reactants can give impetus to the redox reaction, which is the most direct
and effective way to achieve electron transfer.50, 61 Because there is a $\Delta E$ between N-ZnMn$_2$O$_4$/VG and O$_2$, the oxidation of manganese ions and removal of zinc ions in N-ZnMn$_2$O$_4$/VG will be able to happen spontaneously in the system, which includes oxygen dissolved in 4 M Zn(CF$_3$SO$_3$)$_2$ electrolyte. As a result, the completely discharged N-ZnMn$_2$O$_4$/VG may restore to the charged N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG again without external power, and this can be thought of as a chemical self-charging process. When the charged N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG is directly used as the cathode for zinc ion batteries, the $\Delta E$ between the cathode and anode will drive the discharge reaction. In this process, the Zn electrode loses two electrons and becomes Zn$^{2+}$ inserted into N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG, and the electrons move from the negative electrode to the positive electrode through the external circuit to keep charge balance. This system can collect chemical energy from the surrounding environment through chemical self-charging, and then convert the chemical energy into electrical energy for storage, which realizes energy collection, conversion, and storage at the same time. For the sake of exploring self-charging performances, the galvanostatic discharge curves of N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG/Zn batteries with variable oxidation time were first collected. With the increase of oxidation duration, the open-circuit voltage (OCV) of the N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG/Zn batteries continues to rise (Figure 4a, b). This is because with the extension of oxidation time, manganese ions will be oxidized more and more thoroughly, and more and more zinc ions would be extracted from N-ZnMn$_2$O$_4$/VG, leading to higher and higher cathode potential. The OCV of N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG//Zn batteries has a $1.5$ V for the discharge capacity of N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG//Zn batteries can achieve 1.5 V and 1.52 V respectively as the oxidation time lasts to 30 h and 35 h. Apart from OCV, the discharge capacity of N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG//Zn batteries decreases steadily with the extension of oxidation time from 0 to 30 h, and reaches a top capacity of 176.8 mAh g$^{-1}$ at 30 h. These values are much better than that when self-charging in deionized water electrolyte (Figure S11). In addition, even the N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG//Zn batteries in different states, can also show good reversibility during the chemical charging/galvanostatic discharging process. As depicted in Figures 4c and S12, the N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG//Zn batteries with the optimized oxidation time can release 176.8, 162.6, 149.6, 137.6, 126.6 mAh g$^{-1}$ at the current density of 0.1, 0.2, 0.3, 0.4, and 0.5 A g$^{-1}$, respectively. Delightingly, a capacity of 170.2 mAh g$^{-1}$ could be held when the current density was back to 0.1 A g$^{-1}$. Moreover, after 100 cycles, the capacity holding rate of the N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG//Zn batteries is 87.7% for 4 M Zn(CF$_3$SO$_3$)$_2$ electrolyte at 0.1 A g$^{-1}$ (the N-ZnMn$_2$O$_4$/VG electrode is oxidized for 3h), which is superior to that (87.7%) of deionized water electrolyte (Figure 4d and S13), suggesting the superior self-recharge ability and good cyclic stability. Most importantly, this CSCAZIBs can freely switch the charge/discharge modes and work well (Figure 4e). The OCV of the N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG//Zn batteries can steadily achieve 1.28 V after 10 h of chemical self-charging. When the energy in the CSCAZIBs is used up, it can be self-charged again by chemical oxidation. What is even more impressive is that the N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG//Zn batteries could be recharged by the external power supply, which can complete the transition from a self-charged (1.28 V) state or fully discharged (0.8 V) state to the fully charged state (1.8 V).

In order to deeply investigate the reaction mechanism of the chemical self-charging, the structure and composition evolution of the N-ZnMn$_2$O$_4$/x/VG electrode were studied by using all kinds of ex-situ characterization techniques, such as

**Figure 4.** Electrochemical properties of N-Zn$_{1-x}$Mn$_x$O$_{4-x}$/VG/Zn batteries: (a) galvanostatic discharge curves, (b) OCV and discharge capacity at various oxidation time, (c) rate performance, (d) cycle stability (inset is the 20th to 40th cycles), and (e) charging/discharging behavior at hybrid modes.
XPS, XRD, and Raman. The Mn 2p3/2 peak in Figure 5a has an obvious blue-shift with the prolonging of oxidation time from 0 to 35 h. Particularly, a main Mn\textsuperscript{4+} peak is detected, while Mn\textsuperscript{2+} peak disappears and the Mn\textsuperscript{3+} peak obviously weakened in comparison with those of initial N-ZnMn\textsubscript{2}O\textsubscript{4}/VG (Figure 5b), suggesting the oxidation of manganese in N-ZnMn\textsubscript{2}O\textsubscript{4}/VG in this process. In the meantime, the Zn\textsuperscript{2+} ions are extracted from the N-ZnMn\textsubscript{2}O\textsubscript{4}/VG framework, as confirmed by the Raman spectra in Figure 5c. As the oxidation reaction continues, the intensity of the characteristic peaks (301 and 346 cm\textsuperscript{-1}) that relate to the Zn–O bond stretching vibrations gradually decrease. Furthermore, the extractions of Zn\textsuperscript{2+} from ZnMn\textsubscript{2}O\textsubscript{4} would result in the shrinking of the crystal lattice (Figure S14). When the oxidation time is increasing, the (103) and (211) reflections of oxidized N-ZnMn\textsubscript{2}O\textsubscript{4}/VG become obvious blue shift. Based on the Bragg equation, the distance between the reflections of oxidized N-ZnMn\textsubscript{2}O\textsubscript{4}/VG has been summarized as below:

\[
\begin{align*}
N - \text{Zn}_1 - \text{Zn}_2 - O_4 - x/VG + z\text{H}_2O + y\text{Zn}((\text{CF}_3\text{SO}_3)_2\text{O})_2\rightarrow \\
N - \text{Zn}_1 - \text{Zn}_2 - O_4 - x/VG + \text{Zn}_2^2 + ((\text{CF}_3\text{SO}_3)_2\text{O})_2\text{(OH)}_2x
\end{align*}
\]

Conclusions

To sum up, a novel CSCAZIBs with dual electrode has been successfully built by using an elaborate N-ZnMn\textsubscript{2}O\textsubscript{4}/VG cathode. The oxygen defects and nitrogen doping can fast ion/electron transports, create more active sites, and decrease band-gap. Moreover, the interconnected VG arrays provide an omnibearing conductive network, high surface area, large porosity, exceptional electrolyte accessibility, and strong mechanical stability. As a consequence, an aqueous zinc ion device, which assembled with the well-designed N-ZnMn\textsubscript{2}O\textsubscript{4}/VG cathode and zinc plate anode, offers superior zinc ion storage properties with a remarkable specific capacity (222 mAh g\textsuperscript{-1} at 0.1 A g\textsuperscript{-1}) and superior rate capability (61.58% retention from 0.1 to 3 A g\textsuperscript{-1}) along with ultralong durability (92.6% retention after 3000 cycles). Additionally, this aqueous zinc-ion battery also shows a prominent energy density (91.8 Wh kg\textsuperscript{-1}) and power density (27.6 kW kg\textsuperscript{-1}), outperforming the currently existing aqueous zinc-ion battery devices. Importantly, this device can realize self-charging benefit from the spontaneous reaction between the discharged N-ZnMn\textsubscript{2}O\textsubscript{4}/VG electrode and O\textsubscript{2}, and be provided with the functions of energy harvesting, conversion and storage. The as-assembled CSCAZIBs could be up to 1.5 V by entirely dependent on a chemical self-charging process, and achieve a specific capacity as high as 176.8 mAh g\textsuperscript{-1}. Even more significant, the various chemical or/and galvanostatic charging hybrid modes can be well compatible and work properly in this CSCAZIBs. This work proves the feasibility of constructing CSCAZIBs with dual electrode structure, and opens new opportunities for the future self-charging integrated device.

Conflicts of interest

There are no conflicts to declare.

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