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# Ultralong-Lifespan Magnesium Batteries Enabled by the Synergetic Manipulation of Oxygen Vacancies and Electronic Conduction

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receiving increasing attention due to their excellent safety performance and high energy density. However, the sluggish kinetics of  $Mg^{2+}$  in the cathode has become one of the main bottlenecks restricting the development of RMBs. Here, we introduce oxygen vacancies to spherical NaV<sub>6</sub>O<sub>15</sub> cross-linked with carbon nanotubes (CNTs) (denoted as SNVO<sub>X</sub>-CNT) as a cathode material to achieve an impressive long-term cycle life of RMBs. The introduction of oxygen vacancies can improve the electrochemical performance of the NaV<sub>6</sub>O<sub>15-X</sub> cathode material. Besides, owing to the introduction of CNTs, excellent internal/external electronic conduction paths can be built inside the whole



electrode, which further achieves excellent electrochemical performance. Moreover, such a unique structure can efficiently improve the diffusion kinetics of  $Mg^{2+}$  (ranging from  $1.28 \times 10^{-12}$  to  $7.21 \times 10^{-12}$  cm<sup>2</sup>·s<sup>-1</sup>). Simulation calculations further prove that oxygen vacancies can cause  $Mg^{2+}$  to be inserted in  $NaV_6O_{15-X}$ . Our work proposes a strategy for the synergistic effect of oxygen vacancies and CNTs to improve the diffusion coefficient of  $Mg^{2+}$  in  $NaV_6O_{15}$  and enhance the electrochemical performance of RMBs.

**KEYWORDS:** oxygen vacancies,  $NaV_6O_{15}$ , alkali metal pre-intercalation, cathode, diffusion kinetics, rechargeable magnesium batteries, electronic conductivity

## 1. INTRODUCTION

High-safety, long cycle life batteries have received increasing attention, due to the frequent lithium ion battery (LIB) explosion accidents.<sup>1-3</sup> Many researchers have tried to overcome this dilemma by replacing highly reactive lithium with other multivalent metal ions such as Mg<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, etc.<sup>4–8</sup> Among them, RMBs are believed to be a potential energy storage system due to their high security, high energy density, and rich magnesium resources on earth.<sup>9–18</sup> In addition, RMBs can also deliver a high working voltage due to their inherent low electrode potential (-2.37 V vs SHE). Despite the abovementioned advantages, the practical application of RMBs is still limited by many factors.<sup>19-21</sup> One of the biggest bottlenecks is the lack of appropriate cathode materials.<sup>22,23</sup> Compared with Li<sup>+</sup>, the high charge density of divalent Mg<sup>2+</sup> makes it difficult for Mg<sup>2+</sup> to be intercalated into conventional cathode materials. Moreover, the strong interaction between Mg<sup>2+</sup> and the host lattice causes sluggish solid-phase diffusion of Mg<sup>2+</sup>, which causes the rapid capacity decay of batteries.<sup>24</sup>

In 2000, Aurbach's group fabricated a highly reversible RMB system using  $Mo_6S_8$  as the cathode material.<sup>25</sup> However, the limited specific capacity (80 mAh·g<sup>-1</sup>) and low operating

voltage ( $\sim$ 1 V vs Mg<sup>2+</sup>/Mg) hinder its application. To increase energy density, many efforts have been devoted to exploiting novel cathode materials with high working voltage and specific capacity and optimizing the existing cathode materials.<sup>26–34</sup>

Among them, the unique layered  $V_2O_5$  provides intercalated sites for inserting ions. Moreover,  $V_2O_5$  can capture multiple electrons during the discharge process, indicating the high theoretical specific capacity of  $V_2O_5$ . But in RMBs, the diffusion kinetics of  $Mg^{2+}$  is very sluggish in the  $V_2O_5$ electrode.<sup>35,36</sup> To solve this problem, Novak et al. introduced water in the electrolyte to realize the storage capacity of  $Mg^{2+}$ . However, the limited capacity and the side effects between water and the Mg anode hinder the application of this method.<sup>37</sup> To our knowledge, the introduction of metal ions between the layers of layered transition metal oxides can greatly enhance the storage capacity of  $Mg^{2+}$  and achieve

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Figure 1. Schematic illustration of the preparation of the SNVO<sub>X</sub>-CNT composites.

excellent electrochemical performance.<sup>38–42</sup> Interlayer ions can stabilize the material structure and expand the diffusion channel to enhance the diffusion kinetics of Mg<sup>2+</sup>. Recently, Deng et al. proposed manganese-ion-pre-inserted hydrated  $V_2O_5$  to improve the capacity of magnesium storage.<sup>3</sup> Similarly, Xu et al. applied Mg<sub>0.3</sub>V<sub>2</sub>O<sub>5</sub>·1.1H<sub>2</sub>O as the cathode material for RMBs to obtain excellent electrochemical performance, indicating that the ion pre-intercalation is an effective method to enhance the electrochemical performance of RMBs.<sup>38</sup> But the crystal water may be extracted during the electrochemical measurements. Based on our previous research, Na<sup>+</sup>-pre-inserted NaV<sub>6</sub>O<sub>15</sub> without crystal water based on the mechanism of insertion/extraction can result in a good electrochemical performance of RMBs.<sup>42</sup> But due to its low intrinsic electronic conductivity, the long cycle life and rate performance were limited.

Herein, we report an encouraging cathode material of spherical  $NaV_6O_{15-X}$  cross-linked with CNTs for RMBs by introducing oxygen vacancies in the sodium-ion-pre-intercalated transition metal oxides to enhance the storage capacity of Mg<sup>2+</sup>. The internal/external electronic conduction in the whole electrode is greatly improved by the introduction of oxygen vacancies and the CNT network, leading to the fast diffusion kinetics of Mg<sup>2+</sup>. Benefitting from this unique structure, SNVO<sub>X</sub>-CNT exhibits excellent electrochemical performance. Furthermore, simulation calculations further confirm that Mg<sup>2+</sup> is more likely to be inserted into  $NaV_6O_{15-X}$ . Our work further proves that it is a feasible way to construct suitable electrodes with a fast diffusion coefficient for RMBs by introducing vacancies and an electronic conduction network inside the cathode material and proposes a simple synthesis method for achieving this goal.

#### 2. EXPERIMENTAL SECTION

**2.1. Synthesis.** The synthesis method of the precursor  $V_2O_5$  spheres was reported by Yu et al.<sup>43,44</sup> For a typical synthesis, 0.6 mL of VO(OiPr)<sub>3</sub> was added into a mixture of 52 mL of acetone, 12 mL of pyridine, and 0.1 mL of water drop by drop under continuous stirring (600 rpm) for half an hour. The yellow precipitate was collected by centrifugation, washed with acetone several times, and then dried at 60 °C for 24 h. The synthesis of  $V_2O_5$  cross-linked with the CNT precursor ( $V_2O_5$ -CNT) was consistent with that of  $V_2O_5$ , except that 0.2 mL of 10 wt % CNT aqueous dispersion was added to the solution under stirring. For the SNVO<sub>X</sub>-CNT composites,  $V_2O_5$ -CNT and NaNO<sub>3</sub> with a stoichiometric ratio were mixed and ground in an agate mortar. Then, the mixture was calcined at 450 °C for 2 h under an Ar atmosphere. Finally, SNVO<sub>X</sub>-CNT composite products were obtained. As a comparison, NaV<sub>6</sub>O<sub>15</sub> was prepared with commercial  $V_2O_5$  and NaNO<sub>3</sub> by a high-temperature reaction

(CNVO) under an  $O_2$  atmosphere. Spherical  $NaV_6O_{15}$  was prepared with  $V_2O_5$  spheres and  $NaNO_3$  by a high-temperature reaction (SNVO) under an  $O_2$  atmosphere.

**2.2. Material Characterization.** The crystal structure and phase of the products were obtained by X-ray diffraction (XRD, Rigaku Ultima IV). The morphology and microstructure of the samples were obtained using a scanning electron microscope (SEM, Hitachi S-4800) and a high-resolution transmission electron microscope (HRTEM, JEM-2100). Raman spectra were obtained on Renishaw. The X-ray photoelectron spectroscopy (XPS) spectra were acquired using a PHI Quantum 2000. The thermogravimetric analysis (TGA) was performed by an SDT-Q600 thermal analyzer under airflow (25–800 °C). Cyclic voltammetry (CV) was measured by an electrochemical workstation (CHI 1000C, Chenhua).

**2.3. Electrochemical Measurements.** The active composite electrode was prepared by mixing the active material, acetylene black (AB), and poly(vinylidene fluoride) (PVDF) with a weight ratio of 7:2:1. The active carbon electrode served as both the counter electrode and the reference electrode (2.45 V vs  $Mg^{2+}/Mg$ ).<sup>45</sup> Anhydrous 0.5 M  $Mg(ClO_4)_2$  in acetonitrile served as the electrolyte and Celgard 2400 as the separator. The synthesis method of the anhydrous electrolyte was reported in our previous work.<sup>42</sup> The CV tests were performed in the potential range of 1.65–2.95 V vs  $Mg^{2+}/Mg$  at 0.1 mV·s<sup>-1</sup>. Before the galvanostatic intermittent titration technique (GITT) tests, the RMBs were cycled at 50 mA·g<sup>-1</sup> for two cycles. The mass loading of the cathode was 1 mg·cm<sup>-2</sup>. The current density of the GITT test was 50 mA·g<sup>-1</sup>. All of the electrochemical measurements were based on CR2032 coin cells at room temperature and at 1.65–2.95 V vs  $Mg^{2+}/Mg$ .

**2.4. Calculation Methodology.** The DFT calculations are performed using the Vienna ab initio Package (VASP) version 5.4.1 with the Perdew–Burke–Ernzerhof (PBE) functional and the projector augmented wave (PAW) method.<sup>46–48</sup> The planewave kinetic cutoff is set to 520 eV, and Monkhorst–Pack *k*-point mesh  $3 \times 3 \times 2$  is used. The pymatgen package is used to generate the input files. The convergence criteria of ionic relaxation and the electronic step are 0.02 eV·Å<sup>-1</sup> and 0.0022 eV, respectively. We used the LSDA + *U* method to correct the strong correlation effect of d electrons in V atoms with the Hubbard *U* correction  $d = 3.25 \text{ eV.}^{49}$  The valence electron configurations for Na, V, O, and Mg are  $2p^63s^1$ ,  $3p^63d^44s^1$ ,  $2s^22p^4$ , and  $2s^2$ , respectively. The structure of Na<sub>2</sub>V<sub>12</sub>O<sub>28</sub> is obtained by randomly removing two oxygen atoms of Na<sub>2</sub>V<sub>12</sub>O<sub>30</sub>.

The process of magnesium insertion reactions can be written as follows

$$Na_2V_{12}O_{30} + xMg(s) \rightarrow Na_2V_{12}O_{30}Mg_x$$
 (1)

$$Na_2V_{12}O_{28} + xMg(s) \rightarrow Na_2V_{12}O_{28}Mg_x$$
 (2)

The average voltages (V) for eqs 1 and 2 are

$$\overline{V_{1}} = -\frac{\Delta G_{\rm r}}{xzF} = -\frac{E_{\rm Na_{2}V_{12}O_{30}}Mg_{\rm x} - E_{\rm Na_{2}V_{12}O_{30}} - xE_{\rm Mg}}{xzF}$$
(3)



Figure 2. (a) XRD patterns and (b) the Raman spectra of CNVO, SNVO, and SNVO<sub>X</sub>-CNT. (c) XPS spectra of SNVO<sub>X</sub>-CNT and the SNVO powder. The XPS spectra of (d) V 2p and (e) O 1s of the SNVO<sub>X</sub>-CNT and SNVO powders. (f) EPR spectra of SNVO and SNVO<sub>X</sub>-CNT.

$$\overline{V_2} = -\frac{\Delta G_r}{xzF} = -\frac{E_{Na_2V_{12}O_{28}Mg_x} - E_{Na_2V_{12}O_{28}} - xE_{Mg}}{xzF}$$
(4)

where x is the number of magnesium ions and equal to 2 in our case, z is the number of electrons transferred to a  $Mg^{2+}$  (z = 2), and F is the Faraday constant. The reaction free energy  $\Delta G_r = \Delta E_r + P\Delta V_r - T\Delta S_r$  can be approximated by the internal energy change  $\Delta E_r$  (eV) since the contributions of entropy and volume expansion to the voltage are very small.  $E_{Na_2V_{12}O_{30}Mg_2}$ ,  $E_{Na_2V_{12}O_{30}}$ ,  $E_{Na_2V_{12}O_{28}Mg_2}$ , and  $E_{Na_2V_{12}O_{28}}$  are the total energies of  $Na_2V_{12}O_{30}Mg_2$ ,  $Na_2V_{12}O_{30}$ ,  $Na_2V_{12}O_{28}Mg_2$ , and  $Na_2V_{12}O_{28}$ , respectively.  $E_{Mg}$  is the energy of the magnesium metal, which is calculated with a magnesium metal cell  $(R\overline{3}m)$  using the Monkhorst–Pack k-point mesh  $6 \times 6 \times 6$ .

## 3. RESULTS AND DISCUSSIONS

As shown in Figure 1,  $V_2O_5$  spheres wrapped and interconnected by CNTs were obtained through a one-step hydrolysis reaction using VO(OiPr)<sub>3</sub> as the precursor. Excellent internal/external electronic conduction paths can be built inside the whole electrode by introducing CNTs. As shown in Figure S1, the peaks of  $V_2O_5$  are located at 15.5, 20.2, and 21.8°, corresponding to the layer spacing of 0.57, 0.44, and 0.41 nm, respectively, while the peaks of NaV<sub>6</sub>O<sub>15-X</sub> are located at 9.4, 12.2, and 12.9°, corresponding to the layer spacing of 0.94, 0.72, and 0.68 nm, respectively. Therefore, the layer spacing of V<sub>2</sub>O<sub>5</sub> was successfully increased by introducing



Figure 3. (a, b) SEM images of SNVO<sub>X</sub>-CNT. (c) TEM and (d) HRTEM images of the SNVO<sub>X</sub>-CNT powder. (e, f) Elemental mapping of SNVO<sub>X</sub>-CNT.

 $Na^+$  between layers to construct  $NaV_6O_{15-X}$  cross-linked with CNTs through a simple solid-state method.

As shown in Figure 2a, the XRD patterns of the CNVO  $(NaV_6O_{15} prepared by commercial V_2O_5 and NaNO_3)$ , SNVO, and SNVO<sub>x</sub>-CNT can be well-matched with that of the monoclinic NaV<sub>6</sub>O<sub>15</sub> (JCPDS no. 77-0146) without any impurities, indicating that the solid-state method can guarantee the purity of the products, even if CNTs are added. The XRD pattern of the V<sub>2</sub>O<sub>5</sub> precursor is shown in Figure S2. The Raman spectra have also been investigated to verify the introduction of CNTs, as shown in Figure 2b. The Raman spectra of SNVO<sub>x</sub>-CNT composites show the two distinct characteristic peaks of C (at around 1345 and 1591 cm<sup>-1</sup>), corresponding to the D-band and G-band, respectively. 50,51 The XPS spectra of SNVO<sub>x</sub>-CNT and the SNVO powder are illustrated in Figure 2c. These results successfully prove the preparation of the target product. Besides, the XPS spectra of SNVO and SNVO<sub>x</sub>-CNT further analyze the internal differences between the two materials. As shown in Figure 2d, the peaks of V 2p of SNVO<sub>X</sub>-CNT are located at V  $2p_{1/2}$  524.56 eV and V  $2p_{3/2}$  517.23 eV, which are lower than those of SNVO. Through calculation and analysis of the XPS results, the ratio of  $V^{5+}/V^{4+}$  is 4.95 in SNVO, while the ratio of  $V^{5+}/$  $V^{4+}$  is 2.35 in SNVO<sub>x</sub>-CNT, indicating more  $V^{4+}$  in SNVO<sub>x</sub>-CNT. Figure 2e shows the XPS spectra of O 1s. Encouragingly,

a wider peak can be observed at 532.6 eV, suggesting the absence of partial lattice O inside SNVO<sub>X</sub>-CNT, which is consistent with other reports of oxygen vacancy.<sup>52–54</sup> Furthermore, as shown in Figure 2f, SNVO<sub>X</sub>-CNT shows a stronger EPR signal (around g = 2.00), indicating the presence of the oxygen vacancies.<sup>41,42</sup> These results indicate that CNT possesses the capability of reducing a part of V<sup>5+</sup> to V<sup>4+</sup> during the high-temperature calcination process. To maintain the balance of anions and cations inside SNVO<sub>X</sub>-CNT, some lattice oxygen is absent, leading to the formation of oxygen defects.

The SEM images of SNVO<sub>X</sub>-CNT are shown in Figure 3a,b. SNVO<sub>X</sub>-CNT inherits well the spherical morphology of the V<sub>2</sub>O<sub>5</sub> precursor with a diameter of around 300 nm (Figure S3a), and CNTs are interspersed on the surface of SNVO<sub>X</sub>-CNT. Similar to SNVO<sub>X</sub>-CNT, SNVO also maintains a good spherical shape (Figure S3b), while CNVO has large irregular particles (Figure S3c). In addition, as shown in the TEM image (Figure 3c), the cross-linked structure of CNTs and the host material inside SNVO<sub>X</sub>-CNT is clearly captured, indicating the successful establishment of an internal/external electronic conductive network in the whole electrode. The HRTEM image of SNVO<sub>X</sub>-CNT (Figure 3d) shows clear lattice fringes with a spacing of 0.702 nm, corresponding to the (002) plane of NaV<sub>6</sub>O<sub>15</sub>. The increased-layer spacing is the result of Na<sup>+</sup>

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**Figure 4.** (a) Charge–discharge curves of the second cycle of CNVO, SNVO, and SNVO<sub>X</sub>-CNT. (b) CV curves of CNVO, SNVO, and SNVO<sub>X</sub>-CNT. (c) Cycling performance. (d) Rate performance of CNVO, SNVO, and SNVO<sub>X</sub>-CNT. (e) Long-term cycling performance. (f) Comparison of the long cycle life and capacity retention in RMBs. (g) Nyquist plots and the fitted results of CNVO, SNVO, and SNVO<sub>X</sub>-CNT and the equivalent circuit (inset).

pre-intercalation. The energy-dispersive spectroscopy (EDS) mappings of Na, V, O, and C in  $SNVO_X$ -CNT are shown in Figure 3e, verifying the uniform distribution of all elements. Among them, the signal of C is relatively weak, which implies a relatively small content of C. To measure the content of C in

the SNVO<sub>X</sub>-CNT composite, the TGA curve is obtained from thermal analysis (Figure S4). When the temperature is heated to 600 °C, the mass retention rate of the composite is 94.81%, meaning that the content of carbon is 5.19%. The mass of the substance increased significantly after 650 °C. According to



Figure 5. (a) Diffusion coefficient of  $Mg^{2+}$  calculated from GITT curves. (b) Average voltage when  $Mg^{2+}$  is intercalated into  $NaV_6O_{15}$  and  $NaV_6O_{15-\chi 2}$  respectively. (c) Schematic illustration of the synergistic effect of oxygen vacancies and CNTs.

our previous research results, this may be due to the oxidation of  $V^{4+}$  to  $V^{5+}$  during high-temperature calcination under airflow.<sup>33,55</sup>

As expected, the introduction of oxygen vacancies and CNTs enhanced the electrochemical performance of the SNVO<sub>x</sub>-CNT cathode in RMBs. To more intuitively compare the difference between the charge-discharge curves and the CV curves of these three cathode materials, the second cycle of charge-discharge curves and CV curves were selected due to the incompleteness of the first cycle of charge-discharge curves and CV curves. As shown in Figure 4a, notably, SNVO<sub>x</sub>-CNT shows a discharge specific capacity of 160 mAh·  $g^{-1}$  and a charge specific capacity of 159 mAh· $g^{-1}$  at 50 mA· $g^{-1}$ , which are higher than those of CNVO and SNVO. Figure 4b demonstrates the typical CV curves of CNVO, SNVO, and SNVO<sub>X</sub>-CNT at 0.1 mV·s<sup>-1</sup>. Compared to CNVO and SNVO, SNVO<sub>X</sub>-CNT presents higher electrochemical activity. The first five cycles the CV curves of CNVO, SNVO, and SNVO<sub>X</sub>-CNT, respectively, are shown in Figure S5 to further prove their electrochemical properties. In terms of cycling performance, SNVO<sub>X</sub>-CNT has a unique advantage (Figure 4c). Due to the larger particle size of CNVO, the diffusion path of Mg<sup>2+</sup> in the CNVO electrode is longer, leading to the poor kinetics of Mg<sup>2+</sup>. SNVO with a smaller particle size can achieve the initial discharge specific capacity of 96.1 mAh·g<sup>-1</sup> at 50 mA·  $g^{-1}$ , but the capacity retention rate is poor. After 50 cycles, the discharge specific capacity of SNVO decayed to 80 mAh·g<sup>-1</sup>. Impressively, SNVO<sub>X</sub>-CNT can maintain 120 mAh·g<sup>-1</sup> after 180 cycles at 50  $\text{m}\text{A}\cdot\text{g}^{-1}$ . The charge-discharge curves of  $SNVO_x$ -CNT in different cycles are shown in Figure S6. Also, there are some differences in the rate performance of the three

materials, as shown in Figure 4d.  $SNVO_X$ -CNT has a better rate performance than CNVO and NVO. The chargedischarge curves of SNVOx-CNT at different rates are shown in Figure S7. To further verify the cycle stability of SNVO<sub>x</sub>-CNT, electrochemical measurements are performed at 0.1 A·g<sup>-1</sup> (Figure 4e). Comparing the three materials, we find that SNVO<sub>x</sub>-CNT still presents a high capacity of 75.5 mAh· g<sup>-1</sup> after 400 cycles. As a comparison, only CNVO and SNVO have a lower discharge specific capacity and poor cycling stability. Moreover, the initial Coulombic efficiency of SNVO<sub>x</sub>-CNT reached 98%, indicating excellent reversibility. However, only CNVO and SNVO have lower initial Coulombic efficiencies of 52 and 80%, respectively. These results fully verify the superiority of oxygen vacancies and the CNT network of SNVO<sub>x</sub>-CNT. However, the electrochemical performance of this as-synthesized material with the wellknown APC electrolyte for reversible deposition/dissolution of Mg is negligible (about 5 mAh·g<sup>-1</sup>) due to the incompatibility of the electrolyte and the cathode. As shown in Figure S8a, the reversible dissolution/deposition of Mg in APC was proved by the results of the CV test. The electrochemical performance of the as-synthesized material was measured with the APC electrolyte, as shown in Figure S8b. As a result, the electrochemical performance of SNVO<sub>x</sub>-CNT is negligible with the APC electrolyte. As shown in Figure 4f and Table S1, compared with previous studies on the cathode in RMBs, SNVO<sub>X</sub>-CNT has advantages in terms of capacity, cycling stability, and long cycle life.<sup>32-34,39,41,53,56-62</sup>

In addition, electrochemical impedance spectroscopy (EIS) tests of these three batteries were also conducted, as shown in Figure 4g, and the fitted data are listed in Table S2. Owing to

the introduction of oxygen vacancies and the CNT electronic conduction network, SNVO<sub>X</sub>-CNT has the lowest charge transfer resistance ( $R_{ct}$ ) (235.5  $\Omega$ ), indicating the enhancement of Mg<sup>2+</sup> diffusion kinetics in the cathode material. The morphologies of the SNVO<sub>X</sub>-CNT electrodes before and after 50 cycles were also studied to prove the stability of SNVO<sub>X</sub>-CNT electrodes during cycling. As shown in Figure S9, the SNVO<sub>X</sub>-CNT electrode can still maintain its morphology after cycling, which implies that the SNVO<sub>X</sub>-CNT electrode has excellent cycling stability during the electrochemical measurements.

The Mg<sup>2+</sup> storage mechanism in the cathode materials is generally divided into two types: the insertion/extraction reaction and the phase conversion reaction. For example, CuS nanotubes and Cu<sub>2-X</sub>Se are based on the phase conversion reaction, which was proved by the appearance of a new phase during the electrochemical reaction.<sup>63,64</sup> However, the Mg<sup>2+</sup> storage mechanism of VO<sub>X</sub> and NaV<sub>6</sub>O<sub>15-X</sub> is the insertion/ extraction reaction.<sup>42,65</sup> No new phase appears during the insertion/extraction reaction and only some diffraction peaks are shifted, implying that the interplanar spacing changes due to the insertion and extraction of Mg<sup>2+</sup>. Therefore, the electrochemical performance of the SNVO<sub>X</sub>-CNT cathode material depends on the diffusion process of Mg<sup>2+</sup> inside the cathode.

To further figure out the kinetic processes, the electronic conductivity and ionic diffusion coefficient were studied. The electronic conductivities of CNVO, SNVO, and the SNVO<sub>X</sub>-CNT powder were also measured, as shown in Table S3. CNVO and SNVO have a similar electronic conductivity, while the electronic conductivity of SNVO<sub>X</sub>-CNT is an order of magnitude greater than those of CNVO and SNVO, owing to the oxygen vacancies and excellent internal/external electronic conduction paths. <sup>52–54,66</sup>

The ionic diffusion coefficient in the solid phase is also an important parameter in evaluating the electrochemical performance of materials. GITT tests have been performed to measure the ionic diffusion coefficient. The diffusion coefficient of  $Mg^{2+}$  ( $D_{Mg^{2+}}$ ) in the cathode material can be calculated from the experimental data by the following formula

$$D_{\mathrm{Mg}^{2+}} = \frac{4}{\pi\tau} \left(\frac{m_{\mathrm{B}}V_{\mathrm{m}}}{M_{\mathrm{B}}A}\right)^{2} \left(\frac{\Delta E_{\mathrm{S}}}{\Delta E_{\tau}}\right)^{2} \left(\tau \ll \frac{L^{2}}{D_{\mathrm{Mg}^{2+}}}\right)$$
(5)

The diffusion coefficients of Mg<sup>2+</sup> in CNVO, SNVO, and SNVO<sub>x</sub>-CNT during the discharge process are calculated from the GITT curves (Figure S10), as shown in Figure 5a. In Figure S10, SNVO<sub>X</sub>-CNT has the smallest polarization, while CNVO has the largest polarization, which is the cause for the difference in the electrochemical performance among CNVO, SNVO, and SNVO<sub>x</sub>-CNT. In the SNVO<sub>x</sub>-CNT electrode, due to the presence of oxygen vacancies and the introduction of the CNT electronic conduction network, the SNVO<sub>x</sub>-CNT electrode has the smallest polarization. Obviously, from Figure 5a, it can be observed that  $SNVO_X$ -CNT has the highest diffusion coefficient of  $Mg^{2+}$  (ranging from  $1.28 \times 10^{-12}$  to  $7.21 \times 10^{-12}$  cm<sup>2</sup>·s<sup>-1</sup>), and the  $Mg^{2+}$  diffusion coefficient basically does not change with the increase of the discharge depth, indicating that there is enough space for Mg<sup>2</sup> transmission inside SNVO<sub>X</sub>-CNT. For comparison, the diffusion coefficient of  $Mg^{2+}$  in CNVO and SNVO is maintained at a relatively low value. As the depth of discharge increases, the diffusion coefficient of magnesium ions tends to

decrease. Notably, compared with SNVO, the Mg<sup>2+</sup> diffusion coefficient of SNVO<sub>x</sub>-CNT is still maintained at  $1.28 \times 10^{-12}$  $cm^2 \cdot s^{-1}$ , which indicates that oxygen vacancies and the CNT electronic conduction network have great importance in improving the diffusion kinetics of Mg<sup>2+</sup> in the cathode material. To explore the effect of CNTs on the diffusion coefficient of Mg<sup>2+</sup> in SNVO<sub>X</sub>-CNT, the N<sub>2</sub> adsorptiondesorption isotherm curves of SNVO and SNVO<sub>x</sub>-CNT were obtained. As shown in Figure S11, the BET surface area of SNVO<sub>X</sub>-CNT is 20.70 m<sup>2</sup> g<sup>-1</sup> while the BET surface area of SNVO is 2.43 m<sup>2</sup> g<sup>-1</sup>, implying that the larger surface area of SNVO<sub>x</sub>-CNT can promote the diffusion of  $Mg^{2+}$  at the SNVO<sub>x</sub>-CNT electrolyte interface.<sup>67–71</sup> Besides, the electrolyte contact angles of SNVOx-CNT and SNVO were also measured, and the results prove the better electrolyte wettability of the SNVO<sub>x</sub>-CNT electrode. The above results and analysis show that the CNTs play a key role in improving the diffusion coefficient of  $Mg^{2+}$  in the SNVO<sub>x</sub>-CNT electrode.

Simulation calculations were also performed to simulate the insertion of  $Mg^{2+}$  in  $NaV_6O_{15}$  and  $NaV_6O_{15-X}$ . As shown in Figure 5b, when  $Mg^{2+}$  is intercalated into  $NaV_6O_{15-X}$ , the average voltage is 2.23 V, whereas for  $NaV_6O_{15-X}$ , the average voltage is 2.41 V. The higher voltage of  $NaV_6O_{15-X}$  indicates that  $Mg^{2+}$  is more likely to be inserted into the structure of  $NaV_6O_{15-X}$  during the discharge process. The above simulation results and analysis further confirm that oxygen vacancies in the  $NaV_6O_{15-X}$  cathode material can effectively improve the energy density of RMBs.

Figure 5c describes the advantages of such a structural design. The introduction of oxygen vacancies effectively enhances the intrinsic electronic conductivity of the SNVO<sub>X</sub>-CNT and Mg<sup>2+</sup> tends to be inserted into the structure of SNVO<sub>X</sub>-CNT.<sup>52–54,66</sup> At the same time, owing to the CNT electronic conduction network, the outstanding internal/external electronic conduction paths can be further built inside the whole electrode. As a result, the kinetics process is improved directly by such structural design. The above results of electrochemical performance tests and simulation calculation fully show that the synergy of oxygen vacancies and the high conductivity of CNTs play an indispensable role in the long cycle life of SNVO<sub>X</sub>-CNT.

#### 4. CONCLUSIONS

In summary, SNVO<sub>X</sub>-CNT has been synthesized by a simple method as the impressive cathode of RMBs with excellent long-term cycle life.  $NaV_6O_{15}$  with  $Na^+$  pre-intercalation has been verified as a promising cathode for RMBs. Based on NaV<sub>6</sub>O<sub>15</sub>, the introduction of oxygen vacancies further improves the diffusion kinetics of  $Mg^{2+}$ . Therefore,  $SNVO_{X^-}$ CNT shows an excellent discharge capacity. Besides, the unique structure of SNVO<sub>x</sub>-CNT maintains excellent stability in long-term electrochemical measurements. Such outstanding electrochemical results of SNVO<sub>X</sub>-CNT are due to the synergistic effect of oxygen vacancies and the internal/external electronic conductive network. The GITT tests and EIS measurements also confirmed the improvement of the dynamics in the cathode  $(D_{\rm Mg^{2+}} \text{ ranging from } 1.28 \times 10^{-12} \text{ to } 7.21 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1})$ . Simulation calculations also verify that oxygen vacancies can cause Mg2+ to be intercalated into the host lattice of NaV<sub>6</sub>O<sub>15-X</sub>. This work proposes the application of defects in cathode materials for RMBs.

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## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c00170.

XRD patterns; SEM images of CNVO, SNVO, and SNVO<sub>X</sub>-CNT; TG curves of SNVO<sub>X</sub>-CNT; CV curves; charge–discharge curves of SNVO<sub>X</sub>-CNT; SEM images of the SNVO<sub>X</sub>-CNT electrodes before and after 50 cycles; GITT curves of CNVO, SNVO, and SNVO<sub>X</sub>-CNT; N<sub>2</sub> adsorption–desorption isotherms and photographs of the electrolyte contact angles of the electrodes; EIS fitted data; and electronic conductivities of CNVO, SNVO, and SNVO<sub>X</sub>-CNT (PDF)

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#### Notes

The authors declare no competing financial interest.

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