

# High-rate performance magnesium batteries achieved by direct growth of honeycomb-like $V_2O_5$ electrodes with rich oxygen vacancies

Dongzheng Wu<sup>1</sup>, Yichao Zhuang<sup>1</sup>, Fei Wang<sup>1</sup>, Yang Yang<sup>2</sup> (🖂), Jing Zeng<sup>1</sup> (🖂), and Jinbao Zhao<sup>1</sup> (🖂)

<sup>1</sup>College of Chemistry and Chemical Engineering, State-Province Joint Engineering Laboratory of Power Source Technology for New Energy Vehicle,

State Key Laboratory of Physical Chemistry of Solid Surfaces, Engineering Research Center of Electrochemical Technology, Ministry of Education, Collaborative Innovation Center of Chemistry for Energy Materials, Xiamen University, Xiamen 361005, China

<sup>2</sup>School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

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# ABSTRACT

Rechargeable magnesium batteries (RMBs) have emerged as a promising next-generation electrochemical energy storage technology due to their superiority of low price and high safety. However, the practical applications of RMBs are severely limited by immature electrode materials. Especially, the high-rate cathode materials are highly desired. Herein, we propose a dual-functional design of  $V_2O_5$  electrode with rational honeycomb-like structure and rich oxygen vacancies to enhance the kinetics synergistically. The result demonstrates that oxygen vacancies can not only boost the intrinsic electronic conductivity of  $V_2O_5$ , but also enhance the Mg<sup>2+</sup> diffusion kinetics inside the cathode, leading to the good high-rate performance. Moreover, *ex-situ* X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) characterizations reveal that Mg<sup>2+</sup> is mainly intercalated from the (101) plane of  $V_2O_{5-x}$  based on the insertion-type electrochemical mechanism; meanwhile, the highly reversible structure evolution during Mg<sup>2+</sup> insertion/extraction is also verified. This work proposes that the dual-functional design of electrode has a great influence in enhancing the electrochemical performance of cathode materials for RMBs.

# **KEYWORDS**

V2O5, rechargeable magnesium batteries, oxygen vacancies, kinetics, electronic conductivity

# 1 Introduction

Lithium ion batteries (LIBs) have been widely commercialized owing to their high energy density [1, 2]. However, in recent years, the application of large-scale energy storage devices has presented stricter requirements on LIBs in terms of cost and safety [3-6]. Tremendous efforts have been devoted to develop other lowpriced and high security batteries beyond LIBs for large-scale energy storage applications [7-15]. Among them, rechargeable magnesium batteries (RMBs) have attracted unprecedented attention owing to their high theoretical volume specific capacity (3,833 mAh·cm<sup>-3</sup>), low electrode potential (-2.37 V vs. standard hydrogen electrode (SHE)), and rich abundance on earth [16-26]. Despite the above theoretical superiorities of RMBs, the development of RMBs is still hindered by some intrinsic and nonnegligible obstacles [27-36]. One of the most challenging task is to explore suitable cathode materials [37-42]. Differing from Li<sup>+</sup>, divalent Mg<sup>2+</sup> has a stronger charge density, leading to the stronger electrostatic interactions between Mg2+ and the lattice of cathode materials. This inherent characteristic results in the sluggish dynamics of Mg<sup>2+</sup> inside the conventional cathode materials. Therefore, developing cathode materials with fast kinetics of Mg<sup>2+</sup> has become one of the greatest challenges in RMBs [43-47].

RMBs is still Mo<sub>6</sub>S<sub>8</sub> reported by Aurbach et al. [48]. In spite of the remarkable cycling performance, the limited specific capacity (only 80 mAh·g<sup>-1</sup>) and the low working potential (1.1 V vs. Mg<sup>2+</sup>/Mg) hinder its further practical application. Our group proposed a Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C/G cathode with the high operating potential of 2.47 V vs. Mg<sup>2+</sup>/Mg to effectively enhance the energy density of RMBs in 2019 [49]. Despite the higher working voltage of Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C/G, the low discharge capacity of 66 mAh·g<sup>-1</sup> is not satisfactory. To further improve the energy density of RMBs, researchers focused their attention on the metal oxide [50–52]. Among them, V<sub>2</sub>O<sub>5</sub> is concerned by scientists owing to its impressive capacity and high operating potential. Nevertheless, in RMBs, V<sub>2</sub>O<sub>5</sub> failed to show the impressive electrochemical performance because of the strong electrostatic interaction between bivalent Mg<sup>2+</sup> and lattice oxygen of V<sub>2</sub>O<sub>5</sub> [53, 54].

Many efforts have been devoted to enhance the electrochemical performance of  $V_2O_5$  for RMBs. Novak et al. proposed a strategy which introduced H<sub>2</sub>O in electrolyte to enhance the capability of the insertion/extraction of Mg<sup>2+</sup> [55]. The introduction of water can effectively reduce the electrostatic interaction between Mg<sup>2+</sup> and lattice oxygen of the host material to promote the transmission of Mg<sup>2+</sup> in V<sub>2</sub>O<sub>5</sub>. However, limited cycling performance and side reaction between Mg foil and H<sub>2</sub>O hinder

Nowadays, one of the most widely used cathode materials for

Address correspondence to Yang Yang, yangyang@gdut.edu.cn; Jing Zeng, zengjing@xmu.edu.cn; Jinbao Zhao, jbzhao@xmu.edu.cn



the development of this strategy. Besides, Perera et al. utilized poly (ethylene oxide) to enhance the diffusion kinetics of Mg<sup>2+</sup> [56]. Nevertheless, the cycling performance and rate performance are limited. Recently, modification of oxygen vacancies in the crystalline host of electrode materials has been proved to be effective in improving the electrochemical performance by providing abundant active sites and enhanced diffusion rate, which inspired us to use this defect engineering strategy in  $V_2O_5$ for RMBs. For instance, Jin et al. prepared black TiO<sub>2-x</sub> with rich oxygen vacancies to achieve the high-performance RMBs [57]. The oxygen vacancies inside cathode can not only reduce the migration energy barrier of Mg2+, but also improve the conductivity of the cathode material and enhance the rate performance for ions storage. Furthermore, our previous work also proves oxygen vacancies are conducive to the insertion of Mg from the simulation calculations [58].

Here, we propose a binder-free and honeycomb-like V<sub>2</sub>O<sub>5-x</sub> electrode on Ti foil with rich oxygen vacancies (denoted as Ti- $V_2O_{5-x}$ ) for RMBs. The presence of oxygen vacancies in Ti- $V_2O_{5-x}$ electrode can not only increase the intrinsic electronic conductivity of V2O5, but also enhance the diffusion kinetics of Mg<sup>2+</sup>. Besides, the honeycomb-like electrode can increase the contact area between the active material and electrolyte and shorten the transmission path of Mg2+ inside the cathode. Benefitting from the unique structure, the as-prepared Ti-V<sub>2</sub>O<sub>5-x</sub> electrode presents the improved discharge specific capacity, cycling performance, and rate performance. The Mg storage mechanism was investigated by a series of ex-situ characterization analysis. This work demonstrates the introduction of defects can enhance the electrochemical performance of RMBs and proposes a facile approach for preparation of cathode with rich oxygen vacancies.

#### 2 Experimental

#### 2.1 Synthesis of Ti-V<sub>2</sub>O<sub>5-x</sub>

For a typical procedure, 0.3 g NH<sub>4</sub>VO<sub>3</sub> was dissolved in 75 mL water. The solution was heated at 75 °C with vigorous stirring until the color of the solution turned yellowy. Afterward, the hydrochloric acid was added drop by drop to the clear solution to adjust the pH value to 2. After 10 min, the solution was transferred into a Teflon lined stainless steel autoclave and the Ti foil (3 cm × 6 cm × 0.01 mm) was immersed in the mixed solution. Subsequently, the mixture was maintained at 180 °C for 10 h. The Ti-V precursor was washed with water for 3 times, followed by drying at 80 °C. Finally, the Ti-V precursor was calcined under Ar atmosphere at 400 °C for 2 h to obtain Ti-V<sub>2</sub>O<sub>5-x</sub>. In addition, Ti-V<sub>2</sub>O<sub>5</sub> was prepared by the same method except that the Ti-V precursor was calcined in air.

#### 2.2 Materials characterization

The X-ray diffraction (XRD) information was collected by a Rigagku Miniflex 600 X-ray diffractometer. The morphologies were investigated by scanning electron microscopy (SEM, Zeiss Gemini SEM 500) and transmission electron microscope (TEM, Tecnai F30). The X-ray photoelectron spectroscopy (XPS) data were obtained by PHI Quantum 2000. Electrochemical impedance spectra (EIS) were ascertained by a Solartron 1260A and 1287A impedance/gain-phase analyzer.

#### 2.3 Electrochemical measurements

The Ti-V<sub>2</sub>O<sub>5-x</sub> and Ti-V<sub>2</sub>O<sub>5</sub> electrodes were punched into round discs with a diameter of 12 mm to serve as the cathode of RMBs directly. The CR2032 coin cells were assembled including the as-

prepared cathode, 0.5 M Mg(ClO<sub>4</sub>)<sub>2</sub>/acetonitrile electrolyte, Celgard 2400 separator and active carbon electrode counter electrode [59]. The cyclic voltammetry (CV) was operated using the CHI 660E multipotentiostat (Chenhua) at 0.3 mV·s<sup>-1</sup>. And the mass loading of active materials in electrode was about 0.35 mg·cm<sup>-2</sup>. The V<sub>2</sub>O<sub>5-x</sub> and V<sub>2</sub>O<sub>5</sub> powders were scraped from the electrodes with a spatula. For the galvanostatic intermittent titration technique (GITT) tests, the batteries were discharged/charged at 50 mA·g<sup>-1</sup> for 600 s and paused for 1 h. All the EIS were carried out by the full discharge stated cell. All the electrochemical measurements were tested at room temperature.

## 3 Result and discussion

The synthesis process of  $Ti-V_2O_{5-x}$  is shown in Fig. 1(a). First of all, the Ti foil reacted with the solution containing vanadium at 180 °C. After the reaction finished, the honeycomb-like Ti-V precursor was collected, washed and dried. Finally, the Ti-V precursor was calcined at 400 °C under Ar atmosphere to acquire the Ti-V\_2O\_{5-X} with rich oxygen vacancies. The Ti-V\_2O\_5 was prepared by the same method except that the Ti-V precursor was calcined in air. The SEM image of Ti-V precursor is shown in Fig. S1 in the Electronic Supplementary Material (ESM). The SEM images of Ti-V<sub>2</sub>O<sub>5</sub> and Ti-V<sub>2</sub>O<sub>5-x</sub> are shown in Figs. 1(b) and 1(c), respectively. Similar to the morphology of Ti-V precursor, both Ti-V2O5 and Ti-V2O5-X samples have a honeycomb structure while the Ti-V<sub>2</sub>O<sub>5-x</sub> has a smaller pore, indicating the larger specific area of Ti-V<sub>2</sub>O<sub>5-x</sub> and larger contact area between Ti-V<sub>2</sub>O<sub>5-x</sub> electrode and electrolyte. Besides, porosity is an important parameter to measure the specific surface area of materials. The porosities of these two electrodes were calculated based on Eq. (1)

$$P = \left(1 - \frac{\rho_0}{\rho}\right) \times 100\% \tag{1}$$

The optical photographs of thickness tests about  $Ti-V_2O_5$  electrodes and  $Ti-V_2O_{5-X}$  electrodes are shown in Fig. S2 in the ESM. The mass loading is about 0.4 mg. The thickness of the



**Figure 1** (a) Schematic illustration of the synthesis of  $\text{Ti-V}_2\text{O}_{s,x}$  SEM images of (b)  $\text{Ti-V}_2\text{O}_s$  and (c)  $\text{Ti-V}_2\text{O}_{s,x}$  (d) TEM image and (e) HRTEM image of  $\text{V}_2\text{O}_{s,x}$  (f) The elemental mapping of  $\text{Ti-V}_2\text{O}_{s,x}$ .

untreated Ti foil is 0.01 mm. As a result, the thickness of the  $V_2O_5$  is about 0.04 mm and the thickness of the  $V_2O_{5-X}$  is about 0.05 mm. After calculations, the porosity of the Ti- $V_2O_{5-X}$  electrode is 76.25% while the porosity of the Ti- $V_2O_{5-X}$  electrode is 70.31%, indicating the Ti- $V_2O_{5-X}$  electrode has a higher specific surface area. As shown in Figs. 1(d) and 1(e), the TEM image of  $V_2O_{5-X}$  shows the sheet structure of  $V_2O_{5-X}$  and the HRTEM image of  $V_2O_{5-X}$  exhibits clear lattice fringes of 0.339 nm, which matches well with the (101) plane of  $V_2O_{5-X}$  fully proves the uniform distribution of V and O elements in the Ti- $V_2O_{5-X}$  electrode.

Figure 2(a) shows that the XRD patterns of Ti-V<sub>2</sub>O<sub>5-X</sub> electrode and the Ti- $V_2O_5$  electrode are in accordance with  $V_2O_5$  (JCPDS. No. 74-1595) and Ti (JCPDS. No. 05-0682). To further verify the purity of samples, the XRD patterns of Ti-V<sub>2</sub>O<sub>5-x</sub> powder and Ti-V<sub>2</sub>O<sub>5</sub> powder were also obtained. Figure S3 in the ESM exhibits that the XRD patterns of V<sub>2</sub>O<sub>5-X</sub> powder and the V<sub>2</sub>O<sub>5</sub> powder can be well matched with  $V_2O_5$  (JCPDS. No. 74-1595), indicating the successful preparation of pure V<sub>2</sub>O<sub>5</sub> on the Ti foil. Besides, the electron paramagnetic resonance (EPR) spectra of the  $V_2O_{5-X}$ powder and the V2O5 powder were performed to prove the existence of oxygen vacancies. In Fig. 2(b), the  $V_2O_{5-x}$  powder exhibits the significant EPR signal with a g value of 1.95 while the V<sub>2</sub>O<sub>5</sub> powder shows a negligible EPR signal, which indicates that  $V_2O_{5-x}$  has richer oxygen vacancies than  $V_2O_5$ . Moreover, the XPS spectra of  $V_2O_{5-x}$  and  $V_2O_5$  also prove the existence of oxygen vacancies in V2O5-x. As shown in Fig. 2(c), the binding energies of V 2p in  $V_2O_{5-x}$  are lower than those of  $V_2O_5$ , implying more V<sup>4+</sup> in  $V_2O_{5-x}$ . And the XPS of O 1s also provides strong evidence to prove the existence of oxygen vacancies (Fig. 2(d)). The wider peak located at 532.1 eV implies the missing of lattice O inside the V<sub>2</sub>O<sub>5-x</sub>. All the morphology and phase characterizations demonstrate that the honeycomb-like  $Ti-V_2O_{5-X}$  with rich oxygen vacancies has been synthesized successfully.

To evaluate Mg<sup>2+</sup> storage properties of as-prepared Ti-V<sub>2</sub>O<sub>5-x</sub> and Ti-V2O5 samples, various electrochemical measurements were performed. The discharge-charge profiles of Ti-V2O5-X and Ti- $V_2O_5$  are shown in Fig. 3(a). The Ti- $V_2O_{5-x}$  shows the pristine discharge and charge capacities are 241.3 and 240.0 mAh·g<sup>-1</sup>, respectively, corresponding to the initial Coulombic efficiency of 99.46%. However, Ti-V2O3 exhibits the pristine discharge and charge capacities are 182.4 and 163.1 mAh·g<sup>-1</sup>, respectively, corresponding to the initial Coulombic efficiency of 89.42%. Ti-V<sub>2</sub>O<sub>5-x</sub> has not only higher capacity, but also higher Coulombic efficiency, indicating the oxygen vacancies are of great importance to enhance the magnesium storage capacity. Besides, as shown in Fig. 3(b), the first two cycles of CV profiles of Ti-V<sub>2</sub>O<sub>5-X</sub> and Ti- $V_2O_5$  also indicate that the Ti- $V_2O_{5-x}$  electrode shows the higher storage capacity of magnesium. The reversible couple of peaks present the redox of the V5+/V4+ and the small polarization of Ti- $V_2O_{5-x}$  indicates the better rate performance of Ti- $V_2O_{5-x}$ . Figure 3(c) exhibits the cycling performance of two samples at 100 mA·g<sup>-1</sup>. After 400 cycles, the high reversible discharge capacity of 195.4 mAh·g<sup>-1</sup> can be retained in Ti-V<sub>2</sub>O<sub>5-X</sub> with rich oxygen vacancies. However, Ti-V2O5 maintains a discharge capacity of 97.9 mAh·g<sup>-1</sup> after 400 cycles, indicating that the honeycomb-like structure plays an important role in improving the electrochemical performance. As shown in Fig. 3(d), Ti-V<sub>2</sub>O<sub>5</sub> delivers the discharge capacity of 175.9, 138.3, 90.0, 69.2, and 57.2 mAh·g<sup>-1</sup>, respectively, as the current density is stepwise increased from 100, 200, 300, 400, and 500 mA·g<sup>-1</sup>. Specially, when the current density returns to 100 mA·g<sup>-1</sup>, the as-prepared Ti-V<sub>2</sub>O<sub>5</sub> electrode still can deliver the pristine discharge capacity, indicating the advantages of honeycomb-like electrode structural design. Furthermore, the Ti-V<sub>2</sub>O<sub>5-x</sub> electrode combines the honeycomb-like structure with rich oxygen vacancies to achieve more superior rate performance. Ti-



Figure 2 (a) XRD patterns of the Ti-V<sub>2</sub>O<sub>5-X</sub> and Ti-V<sub>2</sub>O<sub>5</sub> (b) EPR spectra of the V<sub>2</sub>O<sub>5-X</sub> and V<sub>2</sub>O<sub>5</sub>. The XPS spectra of (c) V 2p and (d) O 1s of the V<sub>2</sub>O<sub>5-X</sub> and V<sub>2</sub>O<sub>5</sub>.



Figure 3 (a) The discharge – charge profiles of  $Ti-V_2O_{5,x}$  and  $Ti-V_2O_{5,x}$  (b) The first two cycles of CV profiles of  $Ti-V_2O_{5,x}$  and  $Ti-V_2O_{5,x}$  (c) The cycling performance of  $Ti-V_2O_{5,x}$  and  $Ti-V_2O_{5$ 

 $V_2O_{5-x}$  delivers the discharge capacity of 245.4, 205.8, 174.8, 157.0, and 148.0 mAh·g<sup>-1</sup> at 100, 200, 300, 400, and 500 mA·g<sup>-1</sup>, respectively, indicating the faster diffusion kinetics in the Ti-V<sub>2</sub>O<sub>5-x</sub> electrode with rich oxygen vacancies.

To investigate the structural change of Ti-V<sub>2</sub>O<sub>5-x</sub> for the Mg<sup>2+</sup> storage, the ex-situ XRD of Ti-V2O5-X in different states was conducted (Figs. 4(a) and 4(b)). As shown in Fig. 4(c), a new obvious peak around 26.8° appears during the discharge process. The peak can be matched well with the (111) plane of MgV<sub>2</sub>O<sub>5</sub> (JCPDS. No. 89-1245). Besides, the initial peak (101) at 26.1° of  $V_2O_{5-x}$  also shifts to a lower angle of 24.7° when the Ti- $V_2O_{5-x}$  is discharged from the pristine state to 1.75 V vs. Mg<sup>2+</sup>/Mg, implying the increase of the interplanar crystal spacing of  $V_2O_{5-x}$ . These results indicate that this reaction mechanism is based on the intercalation-type Mg2+ storage mechanism and Mg2+ is mainly intercalated from the (101) plane of V2O5-x during the discharge process, leading to the increase in the interlayer spacing (101) and the formation of new MgV<sub>2</sub>O<sub>5</sub> phase. When Ti-V<sub>2</sub>O<sub>5-x</sub> is charged to 3.35 V vs. Mg<sup>2+</sup>/Mg, all the diffraction peaks of the Ti-V<sub>2</sub>O<sub>5-x</sub> electrode return to the pristine state, implying the outstanding structural stability of Ti-V2O5-X during the electrochemical measurements.

To further study the internal reaction mechanism, *ex-situ* XPS spectra were recorded. As shown in Fig. 4(d), the obvious signal of Mg 1s is observed in the full discharged Ti-V<sub>2</sub>O<sub>5-x</sub> electrode, indicating the insertion of Mg<sup>2+</sup>. And the weak characteristic peak of Mg 1s in full charged Ti-V<sub>2</sub>O<sub>5-x</sub> electrode implies the extraction of Mg<sup>2+</sup>. The XPS spectra of V 2p are shown in Fig. 4(e). The peaks located at 517.2 and 524.9 eV can be considered as V<sup>5+</sup> and the peaks located at 515.8 and 523.2 eV can be considered as V<sup>4+</sup>. The XPS spectrum of V 2p of the initial Ti-V<sub>2</sub>O<sub>5-x</sub> shows an obvious signal of V<sup>4+</sup>, indicating the existence of oxygen vacancies in the initial Ti-V<sub>2</sub>O<sub>5-x</sub>. As the discharge reaction progresses, the binding energy of V 2p shifts to a lower energy and the ratio of V<sup>5+</sup>/V<sup>4+</sup> is obviously reduced, representing the successful intercalation of

 $Mg^{2*}$  inside the Ti-V<sub>2</sub>O<sub>5-x</sub> electrode. When the Ti-V<sub>2</sub>O<sub>5-x</sub> electrode is charged to 3.35 V vs.  $Mg^{2*}/Mg$ , the XPS spectrum of V 2p shows a same peak distribution with that of the initial state, implying the remarkable reversibility of Ti-V<sub>2</sub>O<sub>5-x</sub>. Furthermore, as shown in Fig. 4(f), the elemental mapping of the full discharged Ti-V<sub>2</sub>O<sub>5-x</sub> electrode illustrates that all the elements are uniformly distributed, indicating the intercalation of  $Mg^{2*}$  inside the Ti-V<sub>2</sub>O<sub>5-x</sub> electrode during the discharge process.

To get further insights into the changes of crystal structure during electrochemical measurements, TEM images and selected area electron diffraction (SAED) patterns of the Ti-V<sub>2</sub>O<sub>5-x</sub> electrode in different states were also taken. As shown in Fig. 5, the  $Ti-V_2O_{5-x}$  electrode maintains the nanosheet structure during electrochemical measurements. Besides, before cycling, the clear lattice fringes of 0.339 nm can be observed, corresponding to the (101) plane (Fig. 5(b)) and the corresponding SAED image also proves the purity of the Ti- $V_2O_{5-x}$  electrode (Fig. 5(c)). As shown in Fig. 5(e), as Mg<sup>2+</sup> is inserted into the Ti-V<sub>2</sub>O<sub>5-x</sub> electrode, the lattice spacing of (101) plane is increased to 0.359 nm. Meanwhile, the new lattice plane appears, corresponding to the (111) plane of MgV<sub>2</sub>O<sub>5</sub>. As shown in Fig. 5(f), the SAED image of the full discharged Ti-V2O5-x electrode also proves this change of crystal structure. As shown in Figs. 5(h) and 5(i), when the  $Ti-V_2O_{5-x}$ electrode is charged to the full charged state, the lattice spacing of (101) plane and SAED image are in keeping with the pristine electrode, indicating the remarkable structural stability of Ti-V<sub>2</sub>O<sub>5-x</sub> electrode during the electrochemical measurements.

Besides, in order to further verify the structural stability of the  $Ti-V_2O_{5-x}$  electrode, the SEM images of  $Ti-V_2O_{5-x}$  electrode before and after cycling are taken. As shown in Fig. S4(a) in the ESM, the honeycomb-like structure is strong enough to survive from the pressure during battery assembling. And after 50 cycles, as shown in Fig. S4(b) in the ESM, the honeycomb-like structure of the  $Ti-V_2O_{5-x}$  electrode still maintains as the initial state, implying the outstanding structural stability of the  $Ti-V_2O_{5-x}$  electrode during



**Figure 4** (a) The discharge – charge profiles of Ti-V<sub>2</sub>O<sub>5-x</sub>. (b) *Ex situ* XRD patterns of Ti-V<sub>2</sub>O<sub>5-x</sub> electrode. (c) Local enlarged *ex situ* XRD patterns. XPS spectra of initial, discharged and charged Ti-V<sub>2</sub>O<sub>5-x</sub> electrode at (d) Mg 1s and (e) V 2p regions. (f) The corresponding full discharged Ti-V<sub>2</sub>O<sub>5-x</sub> electrode elemental mapping.



Figure 5 (a) TEM image, (b) HRTEM image, and (c) SAED pattern of the initial Ti- $V_2O_{5-x^2}$  (d) TEM image, (e) HRTEM image, and (f) SAED pattern of the discharged Ti- $V_2O_{5-x^2}$  (g) TEM image, (h) HRTEM image, and (i) SAED pattern of the charged Ti- $V_2O_{5-x^2}$ 

#### the electrochemical tests.

The ionic diffusion coefficient inside the electrode plays a key role in cathode materials. To figure out the role of oxygen vacancies inside the Ti-V<sub>2</sub>O<sub>5-xo</sub> GITT measurements were conducted. The diffusion coefficient of  $Mg^{2+}$  ( $D_{Mg}^{2+}$ ) in cathode

materials can be obtained using the following equation

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

where  $m_{\rm B}$  and  $M_{\rm B}$  are the mass loading (about 0.40 mg) and molecular weight (181.88 g·mol<sup>-1</sup>) of  $V_2O_5$ , respectively;  $V_m$  is the molar volume of  $V_2O_5$  (54.18 cm<sup>3</sup>·mol<sup>-1</sup>); A is the surface area of electrode (1.13 cm<sup>2</sup>);  $\Delta E_s$  is the potential difference of the steadystate voltage during the rest process;  $\Delta E_{\tau}$  is the potential change through a discharge pulse without including IR drop; L is the thickness of the electrode (about 50 µm). As shown in Fig. 6(a), the GITT tests of the Ti-V<sub>2</sub>O<sub>5-X</sub> were carried out. After calculating from the GITT results, the value of  $D_{Mg}^{2+}$  is acquired. As shown in Fig. 6(b), the  $D_{Mg}^{2+}$  of Ti-V<sub>2</sub>O<sub>5-X</sub> is in the order of  $10^{-12}$ - $10^{-14}$  cm<sup>2</sup>·s<sup>-1</sup>, which is higher than that of Ti-V<sub>2</sub>O<sub>5</sub>, corroborating that oxygen vacancies have great importance in enhancing the ionic diffusion coefficient. Moreover, the Nyquist plots and fitted results of the Ti-V<sub>2</sub>O<sub>5-x</sub> electrode and Ti-V<sub>2</sub>O<sub>5</sub> electrode were also conducted to get further insights into the kinetics of Ti-V<sub>2</sub>O<sub>5-x</sub> electrode. As shown in Fig. 6(c), obviously, the Ti-V2O5-X electrode displays a lower resistance of charge transfer  $(R_{d})$  of 206.4  $\Omega$  while the  $R_{d}$  of Ti- $V_2O_5$  electrode is 382.6  $\Omega$ . Furthermore, the  $D_{Mg}^{2+}$  of the cathode materials was also measured by the Warburg region according to the following equations

$$D_{\rm Mg^{2+}} = 0.5 \left(\frac{RT}{n^2 F^2 A C A_{\rm w}}\right)^2 \left(w \gg \frac{2D_{\rm Mg^{2+}}}{L^2}\right)$$
(3)

$$z' = R_{\rm s} + R_{\rm ct} + A_{\rm w} w^{-1/2}$$
 (4)

where *R* is the gas constant; *T* is the absolute temperature; *n* is the number of electrons transferred during the first cycle; *F* is the Faraday's constant; *c* is the concentration of  $Mg^{2+}$  in the Ti-V<sub>2</sub>O<sub>5-*x*</sub> electrode. And  $A_w$  is the Warburg coefficient and its value can be calculated by Eq. (3).  $R_s$  is the resistance inside the battery. After calculation, the relevant parameters are shown in Table 1, which is

consistent with the GITT results. The  $D_{Mg}^{2+}$  of as-prepared cathodes in the full discharged state is  $7.64 \times 10^{-14}$  and  $4.96 \times 10^{-14}$  cm<sup>2</sup>·s<sup>-1</sup>, respectively.

Besides, the activation energy of these two samples was calculated with the results of EIS through the following equation

$$1/R_{\rm ct} = A\exp(-E_{\rm a}/RT) \tag{5}$$

where *A* is the frequency factor; *R* is the gas constant, and *T* is the absolute temperature. As shown in Figs. S5(a) and S5(b), the  $R_{\rm ct}$  of Ti-V<sub>2</sub>O<sub>5-*x*</sub> electrode is lower than that of Ti-V<sub>2</sub>O<sub>5</sub> electrode at different temperatures. After calculations, as shown in Fig. S5(c) in the ESM, the  $E_{\rm a}$  for the Ti-V<sub>2</sub>O<sub>5-*x*</sub> electrode is about 10.94 kJ-mol<sup>-1</sup>, which is lower than that for the Ti-V<sub>2</sub>O<sub>5</sub> electrode (22.38 kJ-mol<sup>-1</sup>). The above results prove that the Ti-V<sub>2</sub>O<sub>5-*x*</sub> electrode has the faster kinetics than Ti-V<sub>2</sub>O<sub>5</sub> electrode and oxygen vacancies can effectively enhance the ionic diffusion coefficient of the Ti-V<sub>2</sub>O<sub>5-*x*</sub> electrode.

Furthermore, the electronic conductivities of  $V_2O_5$  and  $V_2O_{5-x}$ powders were also investigated. As shown in Table S1 in the ESM, the electronic conductivity of  $V_2O_{5-x}$  is 2.6 times that of  $V_2O_5$ , indicating that the introducing oxygen vacancies into the Ti- $V_2O_{5-x}$  cathode also can improve the intrinsic electronic conductivity. The improvements of electronic conduction and ionic diffusion coefficient of  $V_2O_{5-x}$  are the key points for enhancing the electrochemical performance of RMBs.

**Table 1**  $R_{cb} A_w$  and  $D_{Mg}^{2+}$  of Ti-V<sub>2</sub>O<sub>5-X</sub> and Ti-V<sub>2</sub>O<sub>5</sub> electrodes

Sample	$R_{\rm ct}\left(\Omega\right)$	$A_{ m w}\left(\Omega{\cdot}s^{-1/2} ight)$	$D_{{}_{\rm Mg}{}^{2+}}$ (cm <sup>2</sup> ·s <sup>-1</sup> )
$Ti-V_2O_{5-X}$	206.4	358.1	$7.64  imes 10^{-14}$
$Ti-V_2O_5$	382.6	412.2	$4.96\times10^{\scriptscriptstyle-14}$



Figure 6 (a) GITT curves of the Ti-V<sub>2</sub>O<sub>5-X</sub> (b) Diffusion coefficients of Mg<sup>2+</sup> in the Ti-V<sub>2</sub>O<sub>5-X</sub> electrode and Ti-V<sub>2</sub>O<sub>5</sub> electrode. (c) Nyquist plots and fitted results of the Ti-V<sub>2</sub>O<sub>5-X</sub> electrode and Ti-V<sub>2</sub>O<sub>5</sub> electrode. (d) The relationship between the real part of impedance and low frequencies.

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#### 4 Conclusion

In summary, in this work, a bind-free and honeycomb-like Ti- $V_2O_{5-x}$  cathode with rich oxygen vacancies was successfully synthesized for RMBs. The Ti-V2O5-X electrode delivers a high discharge capacity of 241.3 mAh·g-1 at 100 mA·g-1 and high Coulombic efficiency during cycling. After 400 cycles, the Ti- $V_2O_{5-x}$  electrode still maintains the high reversible discharge capacity of 195.4 mAh·g<sup>-1</sup>. Moreover, the Ti-V<sub>2</sub>O<sub>5-x</sub> delivers the discharge capacity of 245.4, 205.8, 174.8, 157.0, and 148.0 mAh·g-1 at 100, 200, 300, 400, and 500 mA·g-1, respectively. Interestingly, when the current density returns to 100 mA·g<sup>-1</sup>, the as-prepared Ti-V2O5-x electrode can still deliver the initial discharge capacity and it can continue to cycle stably with the initial discharge capacity, indicating the advantages of electrode structural design of Ti- $V_2O_{5-x}$ . Besides, the insertion-type electrochemical mechanism was also investigated by ex-situ XRD, TEM, and XPS characterizations. More importantly, the importance of oxygen vacancies was confirmed by the measurements of ionic diffusion coefficient and electronic conduction. The presence of oxygen vacancies can not only increase the intrinsic electronic conduction of V<sub>2</sub>O<sub>5</sub>, but also enhance the ionic diffusion coefficient. This work proposes that the engineering of defects plays a vital role in enhancing the electrochemical performance of cathode materials for multivalent batteries.

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