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## Rod-like anhydrous $V_2O_5$ assembled by tiny nanosheets as a high-performance cathode material for aqueous zinc-ion batteries†

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Aqueous zinc-ion batteries offer a low-cost and high-safety alternative for next-generation electrochemical energy storage, whereas suitable cathode materials remain to be explored. Herein, rod-like anhydrous  $V_2O_5$  derived from a vanadium-based metal-organic framework is investigated. Interestingly, this material is assembled by tiny nanosheets with a large surface area of  $218\text{ m}^2\text{ g}^{-1}$  and high pore volume of  $0.96\text{ cm}^3\text{ g}^{-1}$ . Benefiting from morphological and structural merits, this material exhibits excellent performances, such as high reversible capacity ( $449.8\text{ mA h g}^{-1}$  at  $0.1\text{ A g}^{-1}$ ), good rate capability ( $314.3\text{ mA h g}^{-1}$  at  $2\text{ A g}^{-1}$ ), and great long-term cyclability (86.8% capacity retention after 2000 cycles at  $2\text{ A g}^{-1}$ ), which are significantly superior to the control sample. Such great performances are found to derive from high  $Zn^{2+}$  ion diffusion coefficient, large contribution of intercalation pseudocapacitance, and fast electrochemical kinetics. The *ex situ* measurements unveil that the intercalation of  $Zn^{2+}$  ion is accompanied by the reversible  $V^{5+}$  reduction and  $H_2O$  incorporation. This work discloses a direction for designing and fabricating high-performance cathode materials for zinc-ion batteries and other advanced energy storage systems.

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## 1. Introduction

Although lithium-ion batteries (LIBs) have dominated in portable electronics and emerging electric vehicles, their future potential for large-scale energy storage systems is strongly hindered by limited lithium resources, high cost, and safety issues.<sup>1–3</sup> With the advantages of low cost, good safety, and high energy density, aqueous zinc-ion batteries (AZIBs) are becoming an alternative technology to LIBs, especially for large-scale applications.<sup>3–6</sup> On the one hand, zinc element is abundant on the earth, and its metallic form is stable in water and has an approximate redox potential of  $-0.76\text{ V}$  vs. standard hydrogen electrode (SHE), allowing metallic Zn to be directly used as the anode of AZIBs with a large theoretical specific capacity ( $820\text{ mA h g}^{-1}$  and  $5855\text{ mA h cm}^{-3}$ ).<sup>4,7</sup> On the other hand, aqueous electrolytes contribute to better safety, higher ionic conductivity, easier processing, and lower cost in comparison

with organic electrolytes.<sup>5</sup> Despite great advances made for AZIBs in the last several years, AZIBs are still in their infancy, and their development is severely restricted by the unsatisfactory cathode materials, mainly due to heavy mass and high polarization of divalent  $Zn^{2+}$  ion.<sup>1,3</sup>

In recent years, Mn-based oxides (e.g.,  $MnO_2$ ,<sup>8–12</sup>  $Mn_3O_4$ ,<sup>13</sup> and  $ZnMn_2O_4$  (ref. 14)), polyanionic compounds (e.g.,  $Na_3V_2(-PO_4)_2F_3$  (ref. 15) and  $LiV_2(PO_4)_3$  (ref. 16)), Prussian blue analogues,<sup>17</sup> Mo-based compounds (e.g.,  $MoS_2$  (ref. 18)), and organic and polymer compounds (e.g., polyaniline<sup>19–21</sup> and *p*-chloranil<sup>22</sup>) have been investigated as the cathode materials for AZIBs. However, these materials suffer from either low specific capacity or poor rate capability or short life span. Very recently, vanadium oxide, sulfide, and vanadate cathode materials have attracted much attention since Nazar *et al.* reported  $Zn_{0.25}V_2O_5 \cdot nH_2O$  as a high-capacity ( $\sim 300\text{ mA h g}^{-1}$ ) and long-life (1000 cycles) cathode material.<sup>23–31</sup> It is noteworthy that the reversible, stable, and rapid redox reactions associated with vanadium element render these materials highly appealing for AZIBs. For example, Alshareef *et al.* developed hydrated layered  $Mg^{2+}$ -intercalated  $V_2O_5$  ( $Mg_{0.34}V_2O_5 \cdot 0.84H_2O$ ) with a large interlayer spacing of  $13.4\text{ \AA}$ , which enables high capacities of 353 and  $264\text{ mA h g}^{-1}$  at  $0.1$  and  $1\text{ A g}^{-1}$ , respectively.<sup>25</sup> Niu *et al.* reported  $NaV_3O_8 \cdot 1.5H_2O$  nanobelts, which exhibit high capacity of  $380\text{ mA h g}^{-1}$  at  $0.05\text{ A g}^{-1}$  and great capacity retention of 82% over 1000 cycles.<sup>30</sup>

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Among various vanadium-based materials, anhydrous  $V_2O_5$  is of particular interest owing to its simple configuration and high valence state of vanadium that enable more active sites and higher specific capacity.<sup>32–40</sup> That is, anhydrous  $V_2O_5$  is free of cations (e.g.,  $Zn^{2+}$ ,  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ) and  $H_2O$  molecules within its layers, thus possessing higher gravimetric and volumetric specific capacities than other vanadium-based materials in theory, while such characteristic also makes  $Zn^{2+}$  ion uptake difficult due to the limited interlayer space.<sup>34,41,42</sup> For instance, porous  $V_2O_5$  nanofibers prepared by electrospinning and subsequent calcination delivers merely  $319\text{ mA h g}^{-1}$  at a rather low current density of  $0.02\text{ A g}^{-1}$ , which is substantially lower than the theoretical specific capacity ( $\sim 589\text{ mA h g}^{-1}$  based on the two-electron redox center of vanadium) of  $V_2O_5$ .<sup>34</sup> In addition, this  $V_2O_5$  shows low capacities at high current densities, e.g.,  $104\text{ mA h g}^{-1}$  at  $2.94\text{ A g}^{-1}$ .<sup>34</sup> As is widely utilized for electrode materials, tailoring the morphology, size, and porosity is an effective way to address the above-mentioned problem. In the present work, in order to demonstrate the importance of morphology engineering for  $V_2O_5$  cathode material and elucidate its  $Zn^{2+}$  ion uptake mechanism, we focus on rod-like anhydrous  $V_2O_5$  (denoted RA- $V_2O_5$ ) that is fabricated *via* the pyrolysis of MIL-47. MIL-47 is a vanadium-based metal-organic framework (MOF)  $V^{IV}(O)(bdc)$ , in which bdc represents 1,4-benzenedicarboxylate. It is found that RA- $V_2O_5$  possesses micro/nano-hierarchical structure with large specific surface area and high pore volume, consequently displaying great electrochemical performances.

## 2. Experimental

### 2.1. Materials synthesis and characterization

MIL-47 was synthesized according to a previous report.<sup>43</sup> The as-obtained MIL-47 was kept in a furnace at  $350\text{ }^\circ\text{C}$  for 4 h in the air atmosphere, thus producing RA- $V_2O_5$ . The morphology and microstructure were characterized on JEOL JSM-7600F field emission scanning electron microscope (FE-SEM), JEOL JEM-2100UHR transmission electron microscope (TEM), and Quantachrome Autosorb-iQ2-MP  $N_2$  adsorption/desorption analyzer. The crystallographic information, phase purity, and chemical compositions of the samples were collected by Rigaku Ultima IV powder X-ray diffractometer (XRD) with  $Cu K\alpha$  radiation source, Elementar Vario EL Cube elemental analyzer, TA Instruments Q5000 IR thermogravimetric analyzer (TGA), Thermo Scientific DXR Raman Spectrometer with  $\lambda = 532\text{ nm}$  laser excitation, and Kratos AXIS UltraDLD X-ray photoelectron spectrometer (XPS).

### 2.2. Electrochemical measurements

RA- $V_2O_5$ , Super-P carbon black, and polyvinylidene difluoride (PVDF) were mixed in *N*-methylpyrrolidone (NMP) homogeneously at a weight ratio of 7 : 2 : 1 to form a slurry, which was casted on a titanium foil and dried at  $80\text{ }^\circ\text{C}$  for 4 h. Then the titanium foil was pressed at 10 MPa and cut into round pieces (12 mm in diameter) as working electrodes. The mass loading of RA- $V_2O_5$  is  $1.5\text{--}2\text{ mg cm}^{-2}$ . CR2016 coin cells were assembled by a traditional method using glass fiber membrane (Whatman

GF/A), zinc foil (0.25 mm), and 3 M  $Zn(CF_3SO_3)_2$  aqueous solution as the separator, counter electrode, and electrolyte, respectively. The electrochemical performances of coin cells were examined at current densities from 0.1 to  $5\text{ A g}^{-1}$  in the potential window from 0.2 to  $1.6\text{ V}$  vs.  $Zn^{2+}/Zn$  using a LAND CT2001A battery test system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out using a CHI 660E electrochemical workstation. The solubility of RA- $V_2O_5$  in the electrolyte was evaluated by inductively coupled plasma mass spectrometer (ICP-MS).

## 3. Results and discussion

RA- $V_2O_5$  was fabricated through a two-step process (see Fig. 1a). In the first step, MIL-47 was prepared by a facile hydrothermal reaction of  $VOSO_4$  and bdc acid at  $160\text{ }^\circ\text{C}$ .<sup>43</sup> In the second step, the as-obtained MIL-47 was pyrolyzed at  $350\text{ }^\circ\text{C}$  for 4 h in air, thus transforming into RA- $V_2O_5$ . The crystalline phase of RA- $V_2O_5$  was verified by XRD, as shown in Fig. 1b, which matches exactly with the orthorhombic shcherbinaite  $V_2O_5$  with a *Pmmn* space group (JCPDS 41-1426). The intense peaks at  $2\theta = 15.35^\circ$ ,  $20.25^\circ$ ,  $21.68^\circ$ ,  $26.11^\circ$ ,  $31.00^\circ$ , and  $34.30^\circ$  correspond to the (200), (001), (101), (110), (400), and (310) planes of  $V_2O_5$ , respectively. According to the elemental analysis result, the weight percentages of C and H elements are both lower than 0.3% in RA- $V_2O_5$ , indicating RA- $V_2O_5$  is almost free of carbon and water. The anhydrous nature of RA- $V_2O_5$  is also confirmed by the TGA curve in Fig. S1.<sup>†</sup> For comparison, commercial  $V_2O_5$  purchased from Aladdin (denoted C- $V_2O_5$ ) was also investigated as the cathode material for AZIBs. As can be observed from Fig. S2,<sup>†</sup> all the XRD peaks of C- $V_2O_5$  are attributed to shcherbinaite  $V_2O_5$ . It is also seen that the peaks of C- $V_2O_5$  are much sharper than that of RA- $V_2O_5$ , indicative of much lower crystallinity of the latter.

Fig. 1c shows the global SEM image of RA- $V_2O_5$ , revealing a homogeneous rod-like morphology. These rods are around  $1\text{ }\mu\text{m}$  in diameter and have extremely rough surface. It can be clearly seen from Fig. 1d and e that RA- $V_2O_5$  rods consist of interconnected tiny nanosheets with the thickness of 5–15 nm. Notably, there exist sufficient voids among RA- $V_2O_5$  nanosheets, which can considerably facilitate  $Zn^{2+}$  ion diffusion within  $V_2O_5$ , therefore realizing high specific capacity and great rate capability. Besides, these voids can effectively accommodate the volumetric expansion of  $V_2O_5$  upon  $Zn^{2+}$  ion uptake, which is beneficial for cycling stability. The high-resolution (HR) TEM images of RA- $V_2O_5$  nanosheet at the top surface and cross-section are presented in Fig. 1f and g, in which the lattice fringes of 0.337 and  $0.406\text{ nm}$  correspond to the (110) and (101) crystalline planes of shcherbinaite  $V_2O_5$ , respectively. The orientations and locations of these two planes are illustrated in Fig. 1h and the inset of Fig. 1f and g. As for C- $V_2O_5$ , it is comprised by large particles of 200–600 nm in size, as shown in Fig. S3.<sup>†</sup>

Fig. 2a displays Raman spectra of two  $V_2O_5$  samples. They show nearly identical profiles, and are in good consistent with previously reported  $V_2O_5$ .<sup>33,34</sup> Specifically, the nine bands can be divided into three regions, *i.e.*,  $500\text{--}1000\text{ cm}^{-1}$ ,  $200\text{--}500\text{ cm}^{-1}$ ,



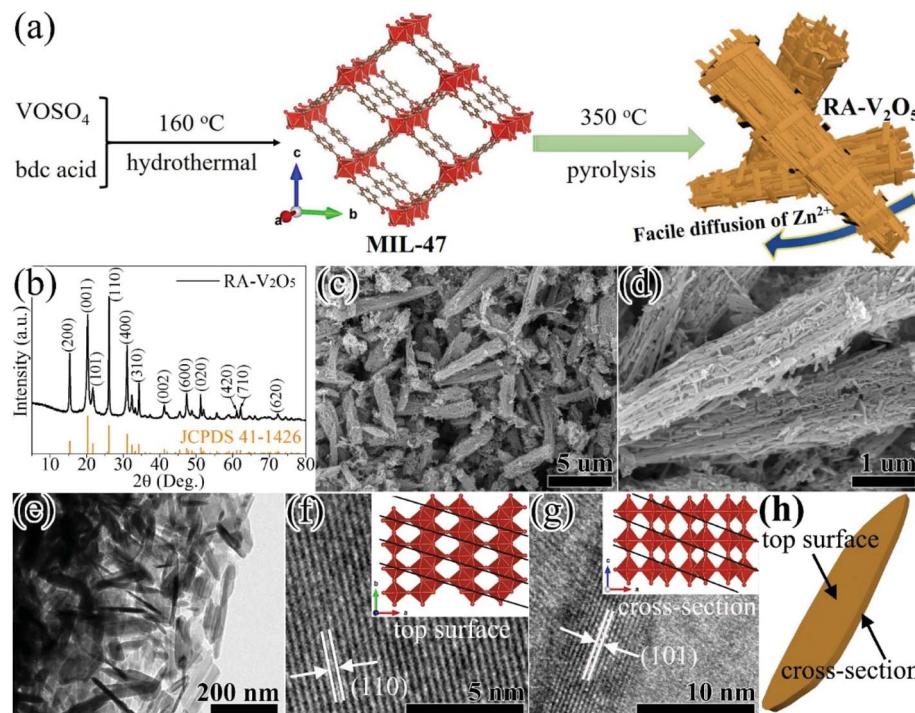


Fig. 1 (a) Schematic illustration of the fabrication process, (b) XRD pattern, (c and d) SEM images, (e–g) TEM images, and (h) illustration of the nanosheet top surface and cross-section of the RA-V<sub>2</sub>O<sub>5</sub>.

and the strongest band at 140 cm<sup>-1</sup>, originating from the bond stretching modes, the angle bending modes, and the shear motion and rotations of the ladders along their axes, respectively.<sup>44</sup> The high purity of RA-V<sub>2</sub>O<sub>5</sub> is also confirmed by its XPS spectrum (Fig. S4†), which only contains peaks belonging to V and O. As for C-V<sub>2</sub>O<sub>5</sub>, a small amount of Na is detected. The existence of sufficient voids within RA-V<sub>2</sub>O<sub>5</sub> is evidenced by N<sub>2</sub> adsorption–desorption analysis. As is shown in Fig. 2b, RA-V<sub>2</sub>O<sub>5</sub> exhibits type IV isotherm (IUPAC classification), indicative of mesoporous structure. According to Brunauer–Emmett–Teller

(BET) theory, the specific surface area of RA-V<sub>2</sub>O<sub>5</sub> is measured to be 218 m<sup>2</sup> g<sup>-1</sup>, much higher than that of C-V<sub>2</sub>O<sub>5</sub> (5.3 m<sup>2</sup> g<sup>-1</sup>). It is worthwhile mentioning that the specific surface area of RA-V<sub>2</sub>O<sub>5</sub> is significantly larger than that of previously reported V<sub>2</sub>O<sub>5</sub> cathode materials for AZIBs, *e.g.*, porous V<sub>2</sub>O<sub>5</sub> nanofibers (27.1 m<sup>2</sup> g<sup>-1</sup>),<sup>34</sup> V<sub>2</sub>O<sub>5</sub> hollow spheres (11.1 m<sup>2</sup> g<sup>-1</sup>),<sup>37</sup> and V<sub>2</sub>O<sub>5</sub> nanofibers (17.9 m<sup>2</sup> g<sup>-1</sup>),<sup>38</sup> therefore making electrolyte permeation and Zn<sup>2+</sup> ion insertion more favourable within RA-V<sub>2</sub>O<sub>5</sub>. Besides, a H<sub>3</sub>-type hysteresis loop is observed for RA-V<sub>2</sub>O<sub>5</sub>, suggesting it is composed of sheet-shaped particles, which

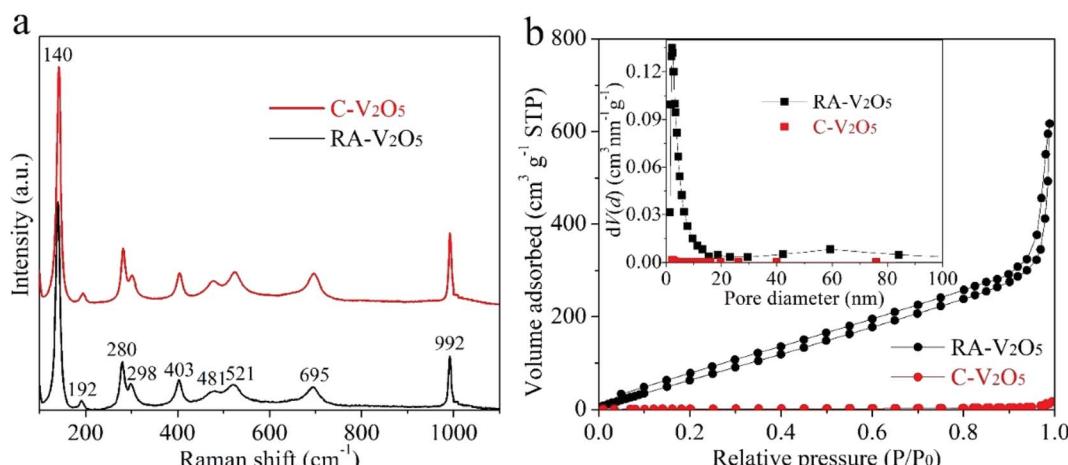


Fig. 2 (a) Raman spectra and (b) N<sub>2</sub> adsorption/desorption isotherms of RA-V<sub>2</sub>O<sub>5</sub> and C-V<sub>2</sub>O<sub>5</sub> (the inset of (b) shows corresponding BJH pore-size distributions).



accords well with its actual morphology observed from TEM. The mesoporous nature of RA-V<sub>2</sub>O<sub>5</sub> is further supported by the Barrett–Joyner–Halenda (BJH) pore size distribution, as shown in the inset of Fig. 2b. In particular, a well resolved peak centered at *ca.* 2.3 nm can be observed. And RA-V<sub>2</sub>O<sub>5</sub> has a large pore volume of 0.96 cm<sup>3</sup> g<sup>-1</sup>, in comparison with merely 0.01 cm<sup>3</sup> g<sup>-1</sup> of C-V<sub>2</sub>O<sub>5</sub>.

The electrochemical properties of RA-V<sub>2</sub>O<sub>5</sub> and C-V<sub>2</sub>O<sub>5</sub> were evaluated in a coin-cell configuration using zinc metal foil and 3 M Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> aqueous solution as the counter/reference electrode and electrolyte, respectively. The CV curves of RA-V<sub>2</sub>O<sub>5</sub> in the initial three cycles at a scan rate of 0.2 mV s<sup>-1</sup> in the potential window of 0.2 to 1.6 V (vs. Zn<sup>2+</sup>/Zn) are shown in Fig. 3a. Multiple pairs of redox peaks can be observed, demonstrating a multistep Zn<sup>2+</sup> ion uptake/release process in V<sub>2</sub>O<sub>5</sub> cathode materials for AZIBs.<sup>36–39</sup> The CV curves of RA-V<sub>2</sub>O<sub>5</sub> at the 1<sup>st</sup> cycle is different from that in the following cycles in terms of peak positions and profiles, behind which the possible reason is the activation of V<sub>2</sub>O<sub>5</sub>. It is also seen that RA-V<sub>2</sub>O<sub>5</sub> exhibits more peaks than C-V<sub>2</sub>O<sub>5</sub> (Fig. S5†) and the peak current densities of RA-V<sub>2</sub>O<sub>5</sub> are much stronger, unveiling that RA-V<sub>2</sub>O<sub>5</sub> has higher electrochemical reactivity than C-V<sub>2</sub>O<sub>5</sub>. Fig. 3b presents the galvanostatic charge/discharge (GCD) curves of RA-

V<sub>2</sub>O<sub>5</sub> in initial three cycles at the current density of 0.1 A g<sup>-1</sup>, in which sloped plateaus can be observed. And the characteristics of these curves are consistent with the above-mentioned CV curves. As for C-V<sub>2</sub>O<sub>5</sub>, its GCD curves (see Fig. S6†) shows similar characteristics, whereas its capacities are much lower than that of RA-V<sub>2</sub>O<sub>5</sub>.

Rate capability is an important parameter for practical applications. Fig. 3c exhibits charge and discharge capacities of RA-V<sub>2</sub>O<sub>5</sub> and C-V<sub>2</sub>O<sub>5</sub> at current densities from 0.1 to 5 A g<sup>-1</sup>. At 0.1 A g<sup>-1</sup>, the discharge capacity of RA-V<sub>2</sub>O<sub>5</sub> rises from 2<sup>nd</sup> cycle gradually, and reaches a maximum value of 464.4 mA h g<sup>-1</sup> at the 13<sup>th</sup> cycle. Such phenomenon is ascribed to the electrochemical activation of V<sub>2</sub>O<sub>5</sub> during Zn<sup>2+</sup> ion storage, which was also observed for previously reported V<sub>2</sub>O<sub>5</sub> cathode materials.<sup>32,34,37,40</sup> The activation is probably related to the poor electrical conductivity of V<sub>2</sub>O<sub>5</sub>,<sup>45</sup> as well as phase transformation and morphology evolution of V<sub>2</sub>O<sub>5</sub> during repeated cycles. This process enables more actives sites that were previously inaccessible to Zn<sup>2+</sup> ions. Then, as the finite activation process becomes slight, the capacity slowly drops to 449.8 mA h g<sup>-1</sup> at the 20<sup>th</sup> cycle. As the current density is raised progressively to 0.2, 0.5, 1, 2, and 5 A g<sup>-1</sup>, the discharge capacity of RA-V<sub>2</sub>O<sub>5</sub> declines to 424.5, 397.8, 361.9, 314.3, and 186.8 mA h g<sup>-1</sup> at the

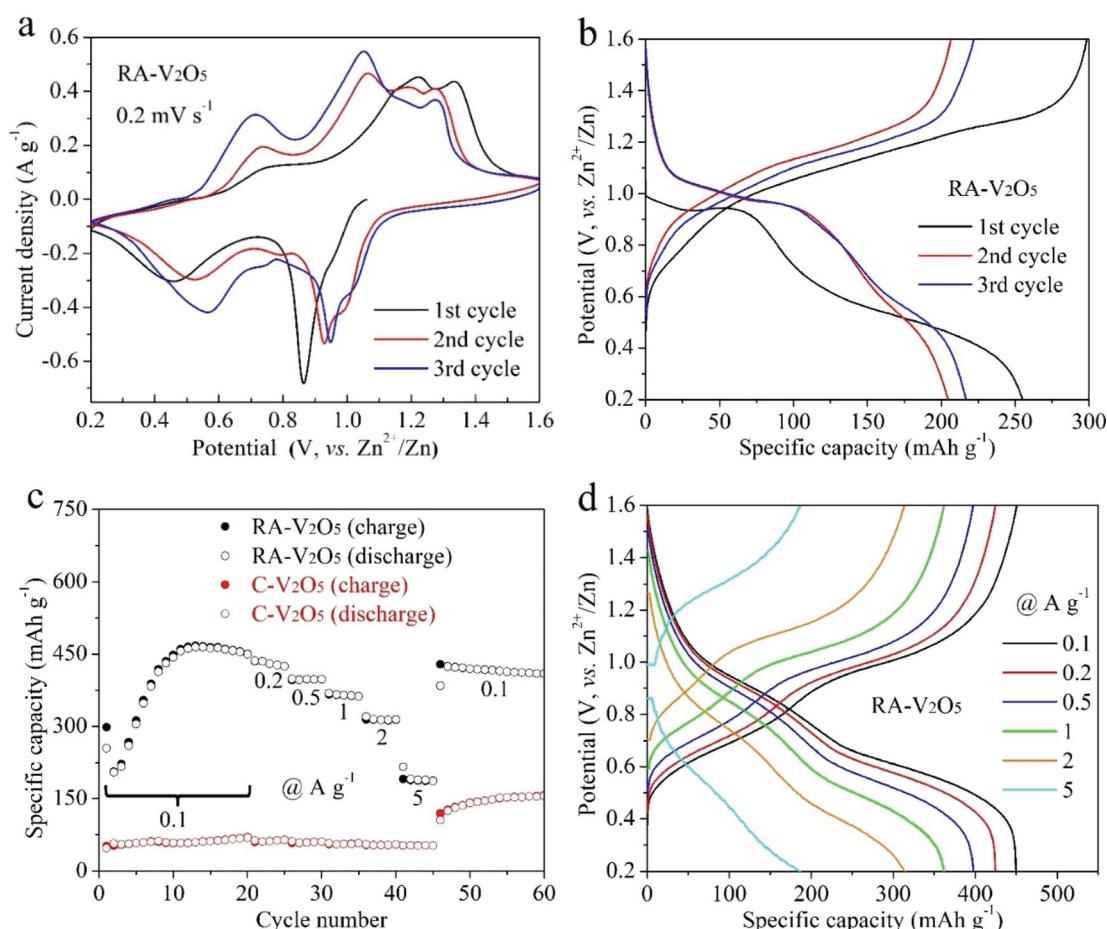


Fig. 3 (a) CV curves of RA-V<sub>2</sub>O<sub>5</sub> in initial three cycles at 0.2 mV s<sup>-1</sup>. (b) GCD curves of RA-V<sub>2</sub>O<sub>5</sub> in initial three cycles at 0.1 A g<sup>-1</sup>. (c) Rate performances of RA-V<sub>2</sub>O<sub>5</sub> and C-V<sub>2</sub>O<sub>5</sub> at current densities from 0.1 to 5 A g<sup>-1</sup>. (d) GCD curves of RA-V<sub>2</sub>O<sub>5</sub> at different current densities.

end of each current density, respectively. When the current density recovers to  $0.1 \text{ A g}^{-1}$ , RA-V<sub>2</sub>O<sub>5</sub> is able to give high capacities between 410 and 420  $\text{mA h g}^{-1}$ , indicative of good electrochemical stability. Besides, it is noted that RA-V<sub>2</sub>O<sub>5</sub> delivers considerably higher capacities than C-V<sub>2</sub>O<sub>5</sub> under all the current densities, manifesting our construction of RA-V<sub>2</sub>O<sub>5</sub> is highly meaningful. Remarkably, thanks to the morphological and structural merits, the RA-V<sub>2</sub>O<sub>5</sub> outperforms many vanadium-based cathode materials reported to date for AZIBs, such as the ones listed in Table S1.† It is clearly seen that our RA-V<sub>2</sub>O<sub>5</sub> is significantly superior to porous V<sub>2</sub>O<sub>5</sub> nanofibers ( $104 \text{ mA h g}^{-1}$  at  $3 \text{ A g}^{-1}$ ),<sup>34</sup> V<sub>2</sub>O<sub>5</sub> nanosheets ( $100 \text{ mA h g}^{-1}$  at  $2 \text{ A g}^{-1}$ ),<sup>36</sup> V<sub>2</sub>O<sub>5</sub> nanospheres ( $138.3 \text{ mA h g}^{-1}$  at  $5 \text{ A g}^{-1}$ ),<sup>39</sup> and V<sub>2</sub>O<sub>5</sub> hollow spheres ( $147 \text{ mA h g}^{-1}$  at  $5 \text{ A g}^{-1}$ ).<sup>37</sup> As is depicted in Fig. 3d, the GCD curve profiles of RA-V<sub>2</sub>O<sub>5</sub> at various current densities display nearly the same shape, implying small polarization and fast electrochemical kinetics.

CV measurements were conducted at various scan rates to study the electrochemical kinetics of RA-V<sub>2</sub>O<sub>5</sub> and C-V<sub>2</sub>O<sub>5</sub>, as displayed in Fig. 4a and b. With the progressive increase of the scan rate from  $0.2$  to  $1.0 \text{ mV s}^{-1}$ , the anodic peaks slightly move to higher potential, while the cathodic peaks shift to the opposite direction. In the meantime, these peaks become broader gradually. This phenomenon is common for electrode

materials, and results from aggravated electrochemical polarization at higher scan rates. When the scan rate is high, the transport of electrons and the diffusion of electrolyte ions in the batteries cannot be synchronized with the quick electron transfer in the external circuit. As a result, the potential/voltage during charging would rise, while the potential/voltage during discharge would decrease. If assuming that the relationship between the scan rate ( $v$ ) and peak current density ( $i$ ) conforms to the following classic power-law equation,<sup>46</sup> the charge storage kinetics can be estimated:

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

where the  $b$  value can be determined from  $\log(i)$  vs.  $\log(v)$  plots (see Fig. S7†) and has been widely used to distinguish different charge storage mechanisms. A  $b$  value of  $0.5$  illustrates the Zn<sup>2+</sup> uptake/release is controlled by the semi-infinite diffusion of Zn<sup>2+</sup> ion, while  $b = 1.0$  indicates surface-induced capacitive charge storage. As can be seen from Fig. 4a, the  $b$  values of the O1, O2, R1, and R2 peaks are fitted to be  $0.89$ ,  $0.86$ ,  $0.71$ , and  $0.83$ , respectively, suggesting the Zn<sup>2+</sup> ion uptake/release is dominated by capacitive behavior, namely pseudocapacitive intercalation proposed by Dunn *et al.*<sup>46</sup> Specifically, the  $b$  values of RA-V<sub>2</sub>O<sub>5</sub> are much larger than that of previously reported

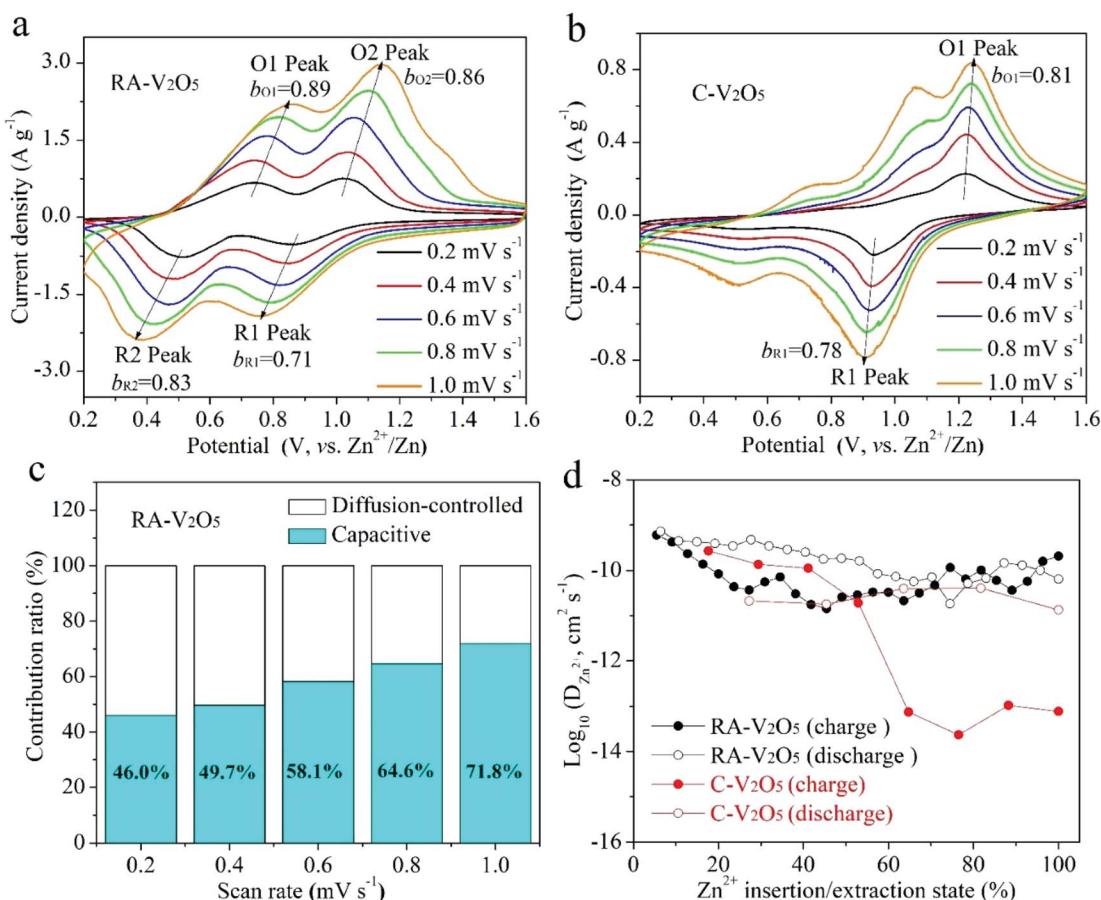


Fig. 4 CV curves of (a) RA-V<sub>2</sub>O<sub>5</sub> and (b) C-V<sub>2</sub>O<sub>5</sub> at various scan rates. (c) Contribution ratios of diffusion-controlled and capacitive capacities of RA-V<sub>2</sub>O<sub>5</sub> at different scan rates. (d)  $D_{Zn^{2+}}$  values of RA-V<sub>2</sub>O<sub>5</sub> and C-V<sub>2</sub>O<sub>5</sub> determined from the GITT method.

$\text{V}_2\text{O}_5$ ,<sup>37,38</sup> meaning that the  $\text{Zn}^{2+}$  ion uptake/release is more favoured in our product. In comparison, the  $b$  values associated with the O1 and O2 peaks of C- $\text{V}_2\text{O}_5$  are calculated to be 0.81 and 0.78, respectively (see Fig. 4b), which are slightly lower than that of RA- $\text{V}_2\text{O}_5$ . However, the peak intensities of C- $\text{V}_2\text{O}_5$  are much lower. In addition, the fraction of the response current density  $i(V)$  that is related to pseudocapacitive intercalation could be calculated according to the following equation:<sup>25,29,47,48</sup>

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

where  $k_1v$  and  $k_2v^{1/2}$  belong to capacitive and diffusion-controlled signals, respectively. The calculation results for RA- $\text{V}_2\text{O}_5$  are displayed in Fig. 4c. It is observed that the contribution ratio of pseudocapacitive intercalation increases from 46.0% to 71.8% when the scan rate rises from 0.2 to 1.0  $\text{mV s}^{-1}$ , confirming that the capacitor-like pseudocapacitive intercalation dominates the charge storage process of RA- $\text{V}_2\text{O}_5$  at high rates. This result elucidates why RA- $\text{V}_2\text{O}_5$  can give great rate performances.

The Galvanostatic Intermittent Titration Technique (GITT) was used to estimate the  $\text{Zn}^{2+}$  ion diffusion coefficients ( $D_{\text{Zn}^{2+}}$ ) in RA- $\text{V}_2\text{O}_5$  and C- $\text{V}_2\text{O}_5$ .<sup>49</sup> Before GITT tests, the coin cells were run at 0.1  $\text{A g}^{-1}$  for 20 cycles to obtain a stable state. Subsequently, a galvanostatic pulse of 1200 s (0.05  $\text{A g}^{-1}$ ) followed by a relaxation of 180 min to allow the potential to reach the equilibrium was repeatedly applied during the whole charge/discharge process. On the basis of the following equation, the  $D_{\text{Zn}^{2+}}$  could be calculated:<sup>23,49</sup>

$$D_{\text{Zn}^{2+}} = \frac{4}{\pi\tau} \left( \frac{n_{\text{M}} V_{\text{M}}}{S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_{\tau}} \right)^2 \quad (3)$$

Although the divalent nature of  $\text{Zn}^{2+}$  ion has an adverse effect on its diffusion within the electrode material, the  $D_{\text{Zn}^{2+}}$  of RA- $\text{V}_2\text{O}_5$  is not low, ranging from  $10^{-9}$  to  $10^{-11} \text{ cm}^2 \text{ s}^{-1}$  (Fig. 4d), which is much higher than  $\text{Li}^+$  ion diffusion in  $\text{LiFePO}_4$  (ref. 50) and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,<sup>51</sup> and higher than  $D_{\text{Zn}^{2+}}$  of previously reported  $\text{V}_2\text{O}_5$ .<sup>38</sup> Besides, the  $D_{\text{Zn}^{2+}}$  of RA- $\text{V}_2\text{O}_5$  is slightly higher than that of C- $\text{V}_2\text{O}_5$  in general, due to much larger specific surface area and pore volume of the former. That is, the ion diffusion at the surface and interface is much more favourable than that within the bulk, therefore contributing to improved rate performances in RA- $\text{V}_2\text{O}_5$ .

Cycling stability is critical for electrode materials. Fig. 5a shows charge and discharge capacities of RA- $\text{V}_2\text{O}_5$  and C- $\text{V}_2\text{O}_5$  during 2000 cycles at 2  $\text{A g}^{-1}$ . The cycling performance tests were conducted after 10 cycles at 0.1  $\text{A g}^{-1}$ . It is seen that the charge capacity is nearly identical to the discharge one at each cycle, implying high coulombic efficiency. In the respect of discharge, RA- $\text{V}_2\text{O}_5$  offers an initial capacity of 317.6  $\text{mA h g}^{-1}$ , which gradually drops to 293.2 and 275.6  $\text{mA h g}^{-1}$  at the 1000<sup>th</sup> and 2000<sup>th</sup> cycle, respectively. That is, the capacity retention of RA- $\text{V}_2\text{O}_5$  is up to 92.3% and 86.8% after 1000 and 2000 cycles, respectively. As for C- $\text{V}_2\text{O}_5$ , its discharge capacity is merely 82.8  $\text{mA h g}^{-1}$  at the 2000<sup>th</sup> cycle, and the corresponding capacity retention is merely 59.4%. After around 30

days (including the period of cycling at 2  $\text{A g}^{-1}$  for 2000 cycles), the electrolyte of RA- $\text{V}_2\text{O}_5$  coin cells was collected by washing the electrodes, separators, and coin cell shells with deionized water. Then the collected electrolyte was subjected to ICP-MS analysis, which reveals only trace amount of vanadium (0.0288%) from RA- $\text{V}_2\text{O}_5$  can be dissolved. Therefore, the active material dissolution is not the main reason of capacity fading for  $\text{V}_2\text{O}_5$  cathode materials. In order to provide more insight into the electrochemical kinetics of RA- $\text{V}_2\text{O}_5$ , EIS measurements were performed using 5 mV amplitude with frequency ranging from 10 mHz to 100 kHz. As is shown in Fig. 5b, the Nyquist plots of RA- $\text{V}_2\text{O}_5$  consist of two parts, *i.e.* a depressed semicircle in the high frequency region (charge transfer process) and a sloped line in the low frequency region (diffusion-limited process).<sup>52</sup> At the initial state, the impedances of RA- $\text{V}_2\text{O}_5$  are considerably lower than that of C- $\text{V}_2\text{O}_5$ , illustrating the morphology engineering adopted by the present study can significantly enhance electrochemical kinetics. Specifically, the charge transfer resistance ( $R_{\text{ct}}$ ) of RA- $\text{V}_2\text{O}_5$  is merely 103.1  $\Omega$ , which gets even smaller (66.8  $\Omega$ ) at the end of 1000 cycles. The reduction of  $R_{\text{ct}}$  might result from activation mentioned in the above section.

The charge storage mechanism of RA- $\text{V}_2\text{O}_5$  was investigated using *ex situ* XRD measurements. The RA- $\text{V}_2\text{O}_5$  electrodes were cycled for 20 times at 0.1  $\text{A g}^{-1}$  to reach a stable state. Subsequently during the 21<sup>th</sup> and 22<sup>th</sup> cycles, the RA- $\text{V}_2\text{O}_5$  electrodes were discharged or charged to a certain state (marked in Fig. 6a). After that, the RA- $\text{V}_2\text{O}_5$  electrodes were separated from the coin cells, rinsed with distilled water thoroughly, and dried under vacuum at room temperature. Herein, carbon black conductive agent was replaced by carbon nanotubes (CNT), so as to avoid the cracking of electrodes during washing with water. Fig. 6b shows XRD patterns of RA- $\text{V}_2\text{O}_5$  at different states. Except for the peaks originating from the Ti current collector and CNT conductive agent (the XRD pattern of neat CNT is shown in Fig. S8†), all the peaks of the electrode at the initial state (before cycles) can be indexed as the shcherbinaite  $\text{V}_2\text{O}_5$ . Surprisingly, all the peaks belonging to  $\text{V}_2\text{O}_5$  disappear after 20 cycles. Instead, several new humps appear and match with  $\text{V}_{10}\text{O}_{24} \cdot 12\text{H}_2\text{O}$ .<sup>53</sup> These new peaks are rather broad and very low in intensity, indicating high-crystalline  $\text{V}_2\text{O}_5$  is electrochemically transformed into amorphous  $\text{V}_{10}\text{O}_{24} \cdot 12\text{H}_2\text{O}$ . When the electrode is discharged to 0.2 V, two new peaks are observed, and then disappear at 1.6 V. These new peaks coincide with the ones for  $\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  at discharged states.<sup>23</sup> In Fig. S9,† some peaks/humps are magnified. It is seen the hump centered at *ca.* 50.4° (corresponding to  $\text{V}_{10}\text{O}_{24} \cdot 12\text{H}_2\text{O}$ ) moves to lower degree during discharging and shifts to higher degree during charging, due to the (de)intercalation of  $\text{Zn}^{2+}$  ions and  $\text{H}_2\text{O}$  molecules. The above results indicate high-crystalline  $\text{V}_2\text{O}_5$  is electrochemically transformed into amorphous  $\text{V}_{10}\text{O}_{24} \cdot 12\text{H}_2\text{O}$  after prolonged cycles. This phenomenon has not been reported for vanadium-based oxide materials before, probably due to that previous reports mainly focused on initial several cycles. In fact, activation process often exists for vanadium-based oxide materials, especially for  $\text{V}_2\text{O}_5$ .<sup>32,34,37,40</sup> In the present study, the rod-like morphology of RA- $\text{V}_2\text{O}_5$  is found to collapse after 2000



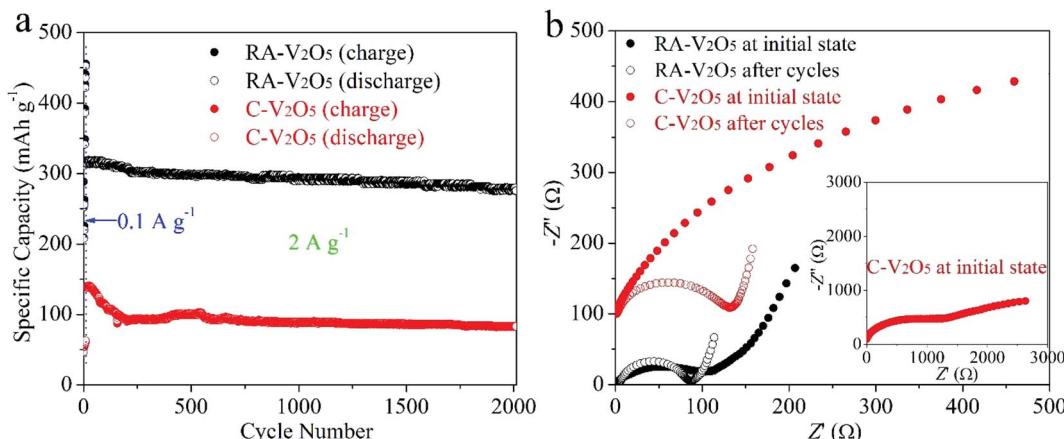


Fig. 5 (a) Cycling performances of RA-V<sub>2</sub>O<sub>5</sub> and C-V<sub>2</sub>O<sub>5</sub> at 2 A g<sup>-1</sup>, conducted after 10 cycles at 0.1 A g<sup>-1</sup>. (b) Nyquist plots of RA-V<sub>2</sub>O<sub>5</sub> and C-V<sub>2</sub>O<sub>5</sub> at initial state and after 1000 cycles at 2 A g<sup>-1</sup>.

cycles at 2 A g<sup>-1</sup>, and in the meantime the nanosheets evolve into interconnected nanowires, as shown in Fig. S10.† Herein, the phase transformation and morphology evolution might account for the activation process of V<sub>2</sub>O<sub>5</sub>.

What's more, the *ex situ* XPS measurements were conducted on RA-V<sub>2</sub>O<sub>5</sub> at the 21<sup>th</sup> cycle, as shown in Fig. 6c-f, in which the spectra were calibrated using the C 1s peak at 284.8 eV. In Fig. 6c, Zn is absent at the initial state. When the electrode is

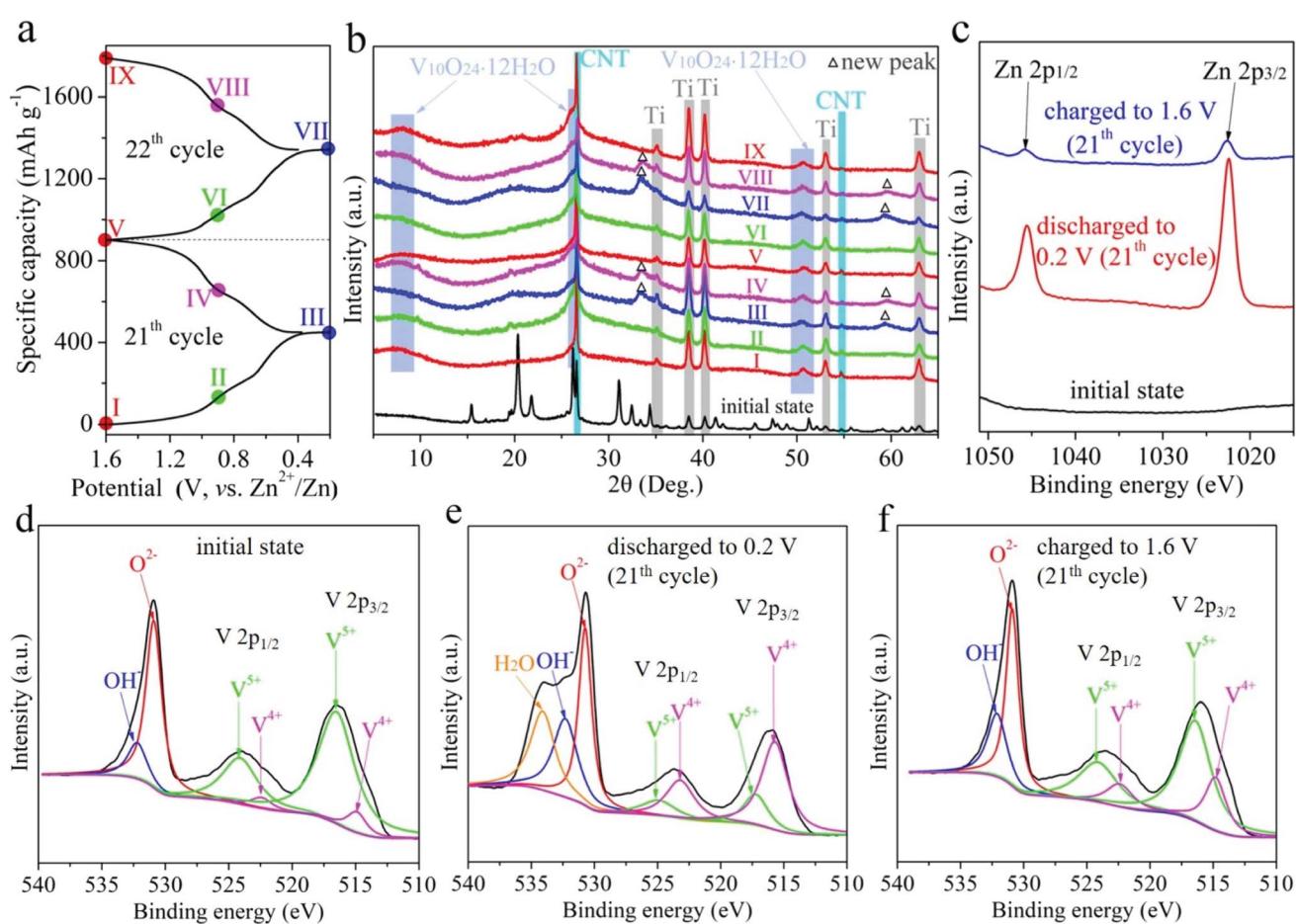


Fig. 6 (a) The GCD curve of RA-V<sub>2</sub>O<sub>5</sub> at 21<sup>th</sup> and 22<sup>th</sup> cycles at 0.1 A g<sup>-1</sup>, presenting nine different charge/discharge states. (b) The *ex situ* XRD patterns of RA-V<sub>2</sub>O<sub>5</sub> at different states. The *ex situ* high-resolution (c) Zn 2p and (d-f) V 2p XPS spectra of RA-V<sub>2</sub>O<sub>5</sub> at the initial state, 0.2 V (21<sup>th</sup> cycle), and 1.6 V (21<sup>th</sup> cycle).



discharged to 0.2 V, two strong peaks corresponding to Zn 2p appear, confirming Zn<sup>2+</sup> is inserted into the host material. When the RA-V<sub>2</sub>O<sub>5</sub> electrode is charged back to 1.6 V, these two peaks are still present, whereas their intensity is far below that for 0.2 V, indicative of good reversibility. The above result also demonstrates that a small amount of inserted Zn<sup>2+</sup> ions cannot be extracted, agreeing well with previous reports.<sup>24,42</sup> This might be the origin of capacity decay. As can be seen from Fig. 6d-f, the V<sup>5+</sup> peak becomes weaker and the V<sup>4+</sup> peak gets stronger when the electrode is discharged, indicating that part of V<sup>5+</sup> is reduced to V<sup>4+</sup> for charge balance. This process is reversible since V<sup>4+</sup> can be oxidized back to V<sup>5+</sup> at 1.6 V. It is also seen that the O 1s subpeak that is assigned to H<sub>2</sub>O is enhanced significantly when the electrode is discharged to 0.2 V, suggesting that H<sub>2</sub>O molecules are incorporated into the host material together with Zn<sup>2+</sup> ion intercalation.<sup>26,28,53</sup> During the charge process, these H<sub>2</sub>O molecules are released. The incorporated H<sub>2</sub>O molecules within the lattice of host material can effectively shield the electrostatic field of Zn<sup>2+</sup> ions that are inserted at the same time, therefore beneficial to electrochemical kinetics.

## 4. Conclusions

Success development of AZIBs mainly depends on the design of cathode materials. In this work, we highlight the importance of morphology engineering by fabricating RA-V<sub>2</sub>O<sub>5</sub> via decomposing MIL-47 at 350 °C in air. Interestingly, RA-V<sub>2</sub>O<sub>5</sub> rods are assembled by tiny nanosheets. Such intriguing morphology and structure endow RA-V<sub>2</sub>O<sub>5</sub> with great performances as the cathode material for AZIBs. It is noticed that the pseudocapacitive Zn<sup>2+</sup> ion intercalation into RA-V<sub>2</sub>O<sub>5</sub> occupies nearly or more than half of the total capacity, *e.g.*, 71.8% at 1 mV s<sup>-1</sup>. RA-V<sub>2</sub>O<sub>5</sub> also possesses high Zn<sup>2+</sup> ion diffusion coefficient of 10<sup>-9</sup> to 10<sup>-11</sup> cm<sup>2</sup> s<sup>-1</sup> and low charge transfer resistance around 100 Ω. The fundamental Zn<sup>2+</sup> ion storage mechanism is also elaborated. The crystalline V<sub>2</sub>O<sub>5</sub> is converted to amorphous V<sub>10</sub>O<sub>24</sub>·12H<sub>2</sub>O and the morphology changes a lot after cycles, which might account for the activation process of V<sub>2</sub>O<sub>5</sub>. And it is found the Zn<sup>2+</sup> ion (de)intercalation is accompanied by the reversible uptake/release of H<sub>2</sub>O molecules and redox transitions between V<sup>5+</sup> and V<sup>4+</sup>. In summary, this work offers a new avenue for designing high-performance cathode materials of AZIBs and reveals a new phenomenon associated with Zn<sup>2+</sup> ion storage.

## Conflicts of interest

There are no conflicts to declare.

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