

Three-Dimensional Interconnected Vanadium Pentoxide Nanonetwork Cathode for High-Rate Long-Life Lithium Batteries

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The continual development of high-performance energy storage devices is critically important for the applications in portable electronics, electric vehicles and renewable largescale energy storages.^[1–3] To meet these demanding applications, rechargeable lithium batteries (LBs) are deemed as one of the best choices owing to their high specific energy and long cycle life.^[4] High specific energy can be achieved by developing electrode materials which have higher specific capacity than current commercial ones.^[5-8] Among the potential cathode materials, vanadium pentoxide (V_2O_5) has been extensively investigated due to its low cost, abundance as well as its high reversible theoretical capacity (about 294 mAh g⁻¹ with 2 Li⁺ ions insertion/extraction per unit formula).^[9-13] Even only one Li⁺ ion insertion/extraction per unit formula. it also can deliver a comparable capacity (147 mAh g^{-1}) compared to the commercialized cathode materials such as $LiCoO_2$ (140 mAh g⁻¹) and $LiMn_2O_4$ (146 mAh g⁻¹).^[14-16] However, two critical issues for this material are its low rate performance and limited long-term cycling stability, owing to the slow electrochemical kinetics and poor structure stability.[17-19]

Constructing nanosized vanadium oxides is considered as one of the most promising directions to facilitate the electrochemical reaction kinetics as well as to mitigate the structure deterioration during cycling, due to the largely increased surface-to-volume ratio, shortened ion diffusion distance, and facile strain relaxation.^[18–22] Various reported works on nanostructure materials with enhanced performance demonstrated that the characteristics, such as

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size, morphology, porosity, and texture, are critically important for the electrochemical performance.^[18–25] Thus, the design and synthesis of suitable nanostructure are the keys to further improve the electrochemical performance. Nanowire/ nanorod provides a direct current pathway for the electrode, improving the charge transport during cycling.^[26,27] In addition, nanowire/nanorod with shortened ion diffusion distance facilitates the ion diffusion kinetics, resulting in the enhanced rate performance.^[27–29]

In the previous work, we reported the ultralong hierarchical V₂O₅ nanowires constructed from attached/interconnected nanorods. Their self-aggregation was reduced due to the nanorod-in-nanowire structure, which results in the large enhanced electrochemical performance.^[27] Herein, we propose that constructing nanowires/nanorods into 3D interconnected porous networks would facilitate the electron/ ion transport and enhance the structure stability, as shown in Scheme 1. The interconnected structures could ensure the electron transport among the subunits.^[22] The inner porous structure promotes the ion diffusion and buffers the volume change during long-term repeated cycles.^[22,25,30] As a cathode for LBs, this interconnected V2O5 nanonetworks exhibit excellent electrochemical cycling and rate performance with little capacity fading after 1000 charge/discharge cycles at high current densities of 1.0 and 2.0 A g^{-1} .

Traditionally, the preparation of V₂O₅ micro-/nanomaterials involves either some time- and energy-consuming steps or expensive solvents.^[24,31-33] In this work, the 3D interconnected V₂O₅ nanonetworks were synthesized via a facile and energy-saving sol-gel approach followed with low-temperature annealing treatment (Figure 1a). The V_2O_5 sols were chosen as the vanadium source, which have been utilized for the synthesis of vanadium based nanomaterials^[30b] and were pre-prepared through the molten V_2O_5 quenching process (detail synthesis processes are described in the Experimental Section). Inorganic salts were chosen as the gelating agent to curdle the as-prepared V₂O₅ sols. Different from other previous reports with long-time (more than 3 days) hydrolysis and aging processes,^[24,31] the hydrogels consisted of thin nanowires were quickly formed (in 2 h) after the addition of gelating agent. Then, the hydrogels were washed to remove the foreign ions and annealed to form the 3D interconnected nanonetworks.



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Scheme 1. The 3D interconnected nanonetworks provide effective and continuous electron transport, rapid ion diffusion and facile strain relaxation for volume change during the lithiation/delithiation processes.



The photographic, scanning electron microscopic (SEM), and transmission electron microscopic (TEM) images were collected at each synthesis state to investigate the formation process of the interconnected V₂O₅ nanonetworks. The sols turn into hydrogels immediately (Figure 1b) after the gelating agent (NH₄H₂PO₄ solution) was added. The SEM image (Figure 1c) displays that the morphology of obtained hydrogels is composed of thin nanowires with diameters ranging from 10 to 20 nm. After being washed, the hydrogel structure (Figure 1b) and the morphology of nanowires (Figure 1d) are largely remained. After annealing treatment, the as-prepared sample is composed of interconnected nanorods with high porosity (Figure 1e,f). The diameters of the nanorods are ≈20 nm. TEM and high-resolution TEM (HRTEM) were conducted to analyze the substructures of the nanonetworks (Figure 1g). Notably, the nanorods are tightly attached with each other, which forms lots of pores in their inner space.^[24] HRTEM image (Figure 1g) taken from the edge of a nanorod shows clear lattice fringes with spacing of 4.09 Å, which is in agreement with that of the (101) plane of V₂O₅ (JCPDS Card No. 00–041–1426).

X-ray diffraction (XRD) was conducted to identify the crystallographic structure and crystallinity of the assynthesized samples (**Figure 2**a). The diffraction pattern of the dried hydrogel displays three broad peaks centered at 8.1° , 25.5° , and 50.6° , similar to that of previously reported $V_2O_5 \cdot nH_2O$ aerogels.^[31] After annealing at 350 °C in air, all



Figure 1. a) Schematic illustration of the synthesis process of the 3D interconnected V_2O_5 nanonetworks. b) The photographs of the samples obtained at each state: (i) V_2O_5 sols, (ii) hydrogels, (iii) washed hydrogels. c–f) SEM images of the as-precipitated hydrogels c), washed hydrogels d), and the annealed interconnected V_2O_5 nanonetworks e,f), respectively. g) TEM image of the interconnected V_2O_5 nanonetworks; inset is the HRTEM image taken from the edge of a nanorod.





Figure 2. XRD patterns a) and FTIR spectra b) of the nanowire precursor and interconnected V_2O_5 nanonetworks, respectively. c) Nitrogen adsorption-desorption isotherm of the interconnected V_2O_5 nanonetworks; (inset) the corresponding pore-size-distribution curve. XPS spectra of the nanowire precursor and interconnected V_2O_5 nanonetworks. (d) Survey spectrum showing V and O (N only from the precursor) elements emanating from the precursor and V_2O_5 nanonetworks. e,f) XPS spectrum of the V 2p binding energy region of nanowire precursor e) and V_2O_5 nanonetworks f), respectively.

the diffraction peaks can be indexed to the orthorhombic phase V₂O₅ (JCPDS Card No. 00-041-1426) with the lattice parameters of a = 11.5160 Å, b = 3.5656 Å, c = 4.3727 Å, space group: Pmmn. The samples were further characterized by FTIR spectra (Figure 2b). The bands at 3432 and 1619 cm⁻¹ reveal the contained water of the hydrous vanadium oxide nanowire precursor.^[34] The band at 1401 cm⁻¹ indicates the existence of NH_4^+ in the precursor,^[34] which is due to the pre-intercalation of NH_4^+ in the large-spacing layer structure of V₂O₅·nH₂O during the gelation process.^[35] Further the element analysis indicates ≈2.1 wt% of N content in the nanowire precursor, thus the precursor is calculated as $(NH_4)_{0.3}V_2O_5H_2O$ (the amount of H₂O is calculated based on the TG analysis, Figure S1, Supporting Information). After annealing the precursor, the FTIR spectra of orthorhombic V_2O_5 exhibit only V-O-V (506 and 768 cm⁻¹) and V=O (1009 cm⁻¹) stretching modes, while the existence of small peaks at 1619 and 3432 cm⁻¹ are due to the absorbed water. X-ray photoelectron spectroscopy (XPS) was measured to analyze the chemical state of vanadium for both the precursor and the V₂O₅ nanonetworks (Figure 2d-f). The XPS spectrum of the precursor exhibits broad peaks of V 2p3/2 and V 2p1/2 (Figure 2e), which can be divided into two peaks corresponding to V⁴⁺ and V⁵⁺ states.^[36] The existence of V⁴⁺ may be due to the pre-intercalated NH₄⁺ during the synthesis process. After annealing the precursor at 350 °C, the peak of V⁴⁺ disappears (Figure 2f), suggesting that crystal V_2O_5 nanonetworks are transformed into V^{5+} completely. Nitrogen adsorption/desorption isotherm measurement was carried out to investigate the Brunauer-Emmet-Teller (BET) surface area and the porous structure of samples, as shown in Figure 2b.^[25] The BET specific surface area of the 3D interconnected V₂O₅ nanonetworks is 43.3 m² g⁻¹. The Barrett–Joyner–Halenda (BJH) pore-size-distribution curve obtained from the isotherm reveals that the sample contains relatively mesopores (average pore diameter is 26.2 nm) and the pore volume is ≈ 0.302 cm³ g⁻¹.

A large variety of V(V) species are formed in aqueous solutions. The concentration and pH value of the V_2O_5 sols is 0.1 $\,$ m and 3, respectively, indicating that the main $V_{10}O_{26}(OH)^{4-}$ specie in solution.^[37] On the basis of the above results, the formation of interconnected nanonetworks is due to the imbalance of surface charge between the V(V) species in the system and the gelating agent, which largely accelerate the gelation of hydrogels (Equation (1)).^[37,38] Meanwhile, the ions exchange process is conducted during the hydrolyzation and gelation (Equation (2))

$$V_{10}O_{26}(OH)_2^{4-} + 4H^+ + (5n-3)H_2O \rightarrow 5V_2O_5 \cdot nH_2O$$
 (1)

$$V_2O_5 \cdot nH_2O + xNH_4^+ \rightarrow (NH_4)_x V_2O_5 \cdot nH_2O$$
⁽²⁾

Similarly, lots of other agents, such as $(NH_4)_2SO_4$, NH_4Cl , Li_2SO_4 , LiCl, Na_2SO_4 , and K_2SO_4 can accelerate the gelation of the V_2O_5 sols (Figure S2, Supporting Information) as well. The whole synthesis process is simple and can be easily scaled up (Figure S3, Supporting Information). After annealing, the loss of water within the crystal (Figure S1 and Equation (3)) along with the distortion of V–O polyhedron^[38,39] during the recrystallization process lead to the shrinkage and fracture of the ultrathin nanowire precursors (Figure 1d), forming the interconnected V_2O_5 networks (Figure 1e,f)^[27]





Figure 3. The electrochemical performance of interconnected V_2O_5 nanonetworks in the potential range from 2.4 to 4.0 V. a) Cyclic voltammograms at a scan rate of 0.1 mV s⁻¹. Charge–discharge curves of the initial cycle b) and cycling performance c) at the current density of 0.1 A g⁻¹, respectively. d) Rate performance of interconnected V_2O_5 nanonetworks and V_2O_5 particles cathodes.

$$V_2O_5 \cdot nH_2O \rightarrow V_2O_5 + nH_2O \tag{3}$$

When the annealing temperature was increased to 450 °C, the V_2O_5 was obtained but with obvious aggregation due to the fast mass transfer under high temperature (Figure S4, Supporting Information). And its BET surface area is 16.68 m² g⁻¹ and pore volume is 0.034 cm³ g⁻¹, which is smaller than those of the sample annealed at 350 °C. Without the gelating process, V_2O_5 particles were synthesized via directly drying and annealing the V_2O_5 sols, whose BET surface area is only 7.6 m² g⁻¹ with a small pore volume of ≈ 0.039 cm³ g⁻¹ (Figure S5, Supporting Information).

Coin cells were assembled to investigate the electrochemical performance of the samples. Cyclic voltammogram (CV) of the interconnected V₂O₅ nanonetworks was measured at a scan rate of 0.1 mV s⁻¹ in a potential range from 2.4 to 4.0 V (**Figure 3**a). Two main couple cathodic/anodic peaks appear at potentials of 3.36/3.45 and 3.15/3.27 V, corresponding to the phase transformations from α -V₂O₅ to ε -Li_{0.5}V₂O₅ and δ -LiV₂O₅, as expressed in Equations (4) and (5), respectively.^[18]

$$\alpha - V_2O_5 + 0.5Li^+ + 0.5e^- \leftrightarrow \varepsilon - Li_{0.5}V_2O_5 \tag{4}$$

$$\varepsilon - \mathrm{Li}_{0.5}\mathrm{V}_{2}\mathrm{O}_{5} + 0.5\mathrm{Li}^{+} + 0.5\mathrm{e}^{-} \leftrightarrow \delta - \mathrm{Li}\mathrm{V}_{2}\mathrm{O}_{5}$$
(5)

The shapes of the curves in the subsequent scans are almost identical, indicating high reversibility of Li⁺ ions insertion/extraction processes. Initial discharge/charge curves of the V_2O_5 cathodes at a current density of 0.1 A g⁻¹ were measured subsequently, as shown in Figure 3b. Two obvious plateaus are observed, which is consistent with the CV

curves. The initial discharge capacity of the interconnected V_2O_5 nanonetworks is 149 mAh g⁻¹. The cycling performance was further evaluated by long-term galvanostatic discharge/charge testing (Figure 3c). After 100 cycles, the discharge capacity of 145 mAh g⁻¹ is still remained, corresponding to 97.3% of the initial capacity, indicating excellent cyclability. Meanwhile, the coulombic efficiency is maintained at $\approx 100\%$ during the entire cycles, demonstrating high cycling reversibility.

For the applications of LBs, both good rate capability and excellent cyclability are necessary. To evaluate the rate capability, the cathodes were cycled at various rates, ranging from 0.1 to 2.0 A g^{-1} in 2.4–4.0 V (Figure 3d). When the rate increases from 0.1 to 2.0 A g⁻¹, the discharge capacity of the interconnected V2O5 nanonetworks cathode decreases gradually from 149 to 100 mAh g⁻¹. However, the V₂O₅ particles cathode exhibits a similar capacity ($\approx 145 \text{ mAh g}^{-1}$) at 0.1 A g^{-1} , but its capacity quickly decreases to 70 mAh g^{-1} at 2.0 A g^{-1} . The difference in capacity between the two samples at high rate is due to the larger surface area (43.3 $m^2 g^{-1}$) of interconnected nanonetworks than that of the particle $(7.6 \text{ m}^2 \text{ g}^{-1})$, which is good for the rate capability. After the high rate measurement, when the rate is reduced back to 0.1 A g^{-1} , a high discharge capacity of 146 mAh g^{-1} (98.7%) of the initial capacity) is recovered, indicating excellent rate stability. The disordered V₂O₅ nanorods were also prepared by hydrothermal method followed by annealing treatment (Figure S6a, Supporting Information).^[40] However, the capacity of the disordered nanorods (Figure S6b, Supporting Information) was lower than that of the interconnected network and the particles (Figure 3d). The reason may be due to the lower surface area of the nanorods $(4.2 \text{ m}^2 \text{ g}^{-1})$ than



Figure 4. The long cycling performance of interconnected V₂O₅ nanonetworks. a) The cycling performance at high rates of 1.0 and 2.0 A g⁻¹. Charge–discharge curves b) and the AC impedance plots c) after different cycles at 1.0 A g⁻¹, respectively.

that of the as-synthesized interconnected nanonetworks $(43.3 \text{ m}^2 \text{ g}^{-1})$ and the particles $(7.6 \text{ m}^2 \text{ g}^{-1})$. And the disorder nanorods with less porosity, leading to the poor rate capability. This further demonstrates the advantage of the 3D interconnected nanonetwork structure.

Moreover, the long-term cycling performance and related charge-discharge curves of the interconnected V₂O₅ nanonetworks cathodes at high rates of 1.0 and 2.0 A g⁻¹ are shown in Figure 4a,b. The initial specific discharge capacities are 110 and 85 mAh g^{-1} at the rates of 1.0 and 2.0 A g^{-1} , respectively. It could be found that the capacities tended to increase in the initial dozens of cycles, which may be due to the gradual penetration of electrolyte into the interior pores of the interconnected networks wetting the electrolyte-electrode interphase and promoting the electrochemical kinetics during cycling.^[41,42] Remarkably, their capacities can be retained to 106 and 84 mAh g⁻¹ even after 1000 cycles, corresponding to 96.4% and 98.8% of their initial discharge capacities, respectively. The cycling performance at higher current densities (1.0 and 2.0 A g⁻¹) is better than that obtained at lower current density (0.1 A g⁻¹) due to the less Li⁺ ions insertion/extraction with less structure destruction during cycling. Electrochemical impedance spectra (EIS) were measured to provide further insights. As shown in Figure 4c and Table S1 (Supporting Information), the charge transfer resistance $(R_{\rm ct})$ value is reduced from 155 Ω after 10 cycles to 147 Ω after 50 cycles and 153 Ω after 100 cycles, corresponding to the increase of the capacity in the initial cycles (Figure 4a), which is due to the wetting between electrolyte and electrode after cycling promote the charge transfer.^[42] Even after 1000 cycles, no obvious impedance increase is detected, indicating stable interface of the interconnected V2O5 nanonetworks.^[42,43] The electrochemical performance of the interconnected V₂O₅ nanonetworks cathode is better than that



of reported V₂O₅ electrodes in terms of high-rate capability and cycling performance, as listed in Table S2 (Supporting Information).^[33,44–46] When the voltage range is extended to 2.0-4.0 V (Figure S7, Supporting Information), the initial discharge capacity increases to 280 mAh g⁻¹ due to the intercalation of more lithium ions. And the capacity can be retained to 220 mAh g⁻¹ after 100 cycles, corresponding to 78.6% of the initial discharge capacity. The capacity and the cycling performance are also comparable to other previous reports.^[27,48,49] Further, we try to increase the charge-discharge potential range to 2.4-4.5 V (Figure S8, Supporting Information). An initial discharge capacity of 167 mAh g⁻¹ is obtained at 0.1 A g⁻¹. After rapid changes of the current densities, the capacities are still stable at each state, further indicating the structure stability under high-potential operation.

The superior lithium storage ability of interconnected V_2O_5 nanonetworks cathodes is attributed to the unique nanostruc-

ture (Scheme 1). First, the interconnected porous structure with large surface area offers effectrive electrode–electrolyte contact area, shortening the ion diffusion distance. Second, the continuous interconnected nanonetworks provide continuous electron transport, which reduces the charge transfer resistance (≈ 155 vs 281 Ω , Figure 4c and Figure S9, Supporting Information) and enhances the rate capability. Third, the existence of pores in networks not only facilitates rapid ion kinetics, but also accommodates the strain induced by the volume change, which ensures a stable structure in some degree during cycling, thus the high-rate long-life performance is obtained (Figure 4).

In summary, a facile and energy-saving approach has been successfully developed to prepare 3D interconnected V₂O₅ nanoworks. The as-synthesized V2O5 nanoworks are consisted of nanorods with diameters around 20 nm. This kind of interconnected 3D networks exhibit a high surface area and large pore volume. When evaluated as a cathode for LBs, the interconnected V₂O₅ nanoworks provide continuous electron transport, rapid ion diffusion, and facile strain relaxation for volume change during lithiation/delithiation processes, leading to relatively high-capacity retention (capacity retention of 97.3% after 100 cycles at 0.1 A g^{-1}). Particularly, they show excellent high-rate cycling capability, with 96.4% and 98.8% capacity retention after 1000 cycles at 1.0 and 2.0 A g⁻¹. The excellent electrochemical performance indicates the promising applications of unique 3D interconnected nanonetworks structure for LBs and other energy storage systems.

Experimental Section

Materials Synthesis: V_2O_5 , $NH_4H_2PO_4$, and other chemical reagents were analytical pure and purchased from Sinopharm



Chemical Reagent Co., Ltd. First, the V₂O₅ sols were prepared by melt quenching process according to previous work.^[50] In brief, V_2O_5 powder (30 g) was placed in a ceramic crucible and heated in air at 800 °C for 20 min at a rate of 10 °C min⁻¹, resulting in a molten liquid. Then, the molten liquid was quickly poured into distilled water (1 L) with stirring, and suspension was obtained. The suspension was heated to the boiling point of water beforehand and then cooled to room temperature naturally. Finally, the suspension was filtered and the brownish V_2O_5 sols were obtained. The concentration of the V_2O_5 sols was calculate by weighting the residual mass after drying the sols in 180 °C for 1 day. To adjust the concentration of sols, moderate distilled water was slowly added and the sols were stirred for another one hour. For the synthesis of V_2O_5 nanonetwoks, $NH_4H_2PO_4$ solution (30 mL, 0.2 M) was added into the pre-prepared V_2O_5 sols (10 mL, 0.1 M) to form the hydrogels. After aging for 2 h, the hydrogels were washed by water and ethanol several times. Then, the washed hydrogels were dried and annealed in air at 350 °C for 2 h at a rate of 2 °C min⁻¹ to obtain the interconnected V₂O₅ nanonetworks. As a control experiment, V₂O₅ particles were synthesized by directly drying at 80 °C and annealing the V_2O_5 sols in the same conditions.

Materials Characterization: XRD measurements were performed to investigate the crystallographic information using a D8 Advance X-ray diffractometer with non-monochromated Cu K α X-ray source. Fourier transformed infrared (FTIR) transmittance spectra were recorded using the 60-SXB IR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were obtained using a VG MultiLab 2000 instrument. TG analysis was performed using NETZSCH-STA449c/3/G thermoanalyzer. N content analysis was determined by Vario EL cube CHNSO elemental analyzer. Brunauer-Emmet-Teller (BET) surface areas were measured by using Tristar II 3020 instrument. The morphology and structure of the product were observed through field emission scanning electron microscopy (SEM, JEOL-7100F). Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were recorded by using a JEM-2100F microscope.

Electrochemical Measurements: The electrochemical properties were evaluated by assembly of 2025 coin cells in an argon-filled glove box ($O_2 \le 1$ ppm and $H_2O \le 1$ ppm). Lithium pellets (China Energy Lithium Co., Ltd.) were used as the anode. 1 M solution of LiPF₆ in ethylene carbon (EC)/dimethyl carbonate (DMC) was used as electrolyte. The cathodes were obtained with 70% active material, 20% acetylene black and 10% poly(tetrafluoroethylene) (PTFE). Then the mixed clay was rolled using a roller mill to form the freestanding film. And the film was cut into disk with a diameter of 8 mm. The loading of the active materials was 2–3 mg cm⁻². Galvanostatic charge/discharge cycling was studied with a multichannel battery testing system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy were tested with an electrochemical workstation (Autolab PGSTAT 302N).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.



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