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Vanadium-based nanostructure materials for secondary lithium battery applications

Abstract

Vanadium-based materials, such as V_2O_5 , LiV_3O_8 , $\text{VO}_2(\text{B})$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ are compounds that share the characteristic of intercalation chemistry. Their layered or open frameworks allow facile ion movement through the interspaces, making them promising cathodes for LIB applications. To bypass bottlenecks occurring in the electrochemical performances of vanadium-based cathodes that derive from their intrinsic low electrical conductivity and ion diffusion coefficients, nano-engineering strategies have been implemented to "create" newly emerging properties that are unattainable at the bulk solid level. Integrating this concept into vanadium-based cathodes represents a promising way to circumvent the aforementioned problems as nanostructuring offers potential improvements in electrochemical performances by providing shorter mass transport distances, higher electrode/electrolyte contact interfaces, and better accommodation of strain upon lithium uptake/release. The significance of nanoscopic architectures has been exemplified in the literature, showing that the idea of developing vanadium-based nanostructures is an exciting prospect to be explored. In this review, we will be casting light on the recent advances in the synthesis of nanostructured vanadium-based cathodes. Furthermore, efficient strategies such as hybridization with foreign matrices and elemental doping are introduced as a possible way to boost their electrochemical performances (e.g., rate capability, cycling stability) to a higher level. Finally, some suggestions relating to the perspectives for the future developments of vanadium-based cathodes are made to provide insight into their commercialization.

Keywords

battery, lithium, applications, secondary, vanadium, materials, nanostructure

Disciplines

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Vanadium-based nanostructure materials for secondary lithium battery applications

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Tuti Mariana Lim^{*d}

Vanadium-based materials, such as V_2O_5 , LiV_3O_8 , $VO_2(B)$ and $Li_3V_2(PO_4)_3$ are compounds that share the characteristic of intercalation chemistry. Their layered or open frameworks allow facile ion movement through the interspaces, making them promising cathodes for LIB applications. To bypass bottlenecks occurring in the electrochemical performances of vanadium-based cathodes that derive from their intrinsic low electrical conductivity and ion diffusion coefficients, nano-engineering strategies have been implemented to "create" newly emerging properties that are unattainable at the bulk solid level. Integrating this concept into vanadium-based cathodes represents a promising way to circumvent the aforementioned problems as nanostructuring offers potential improvements in electrochemical performances by providing shorter mass transport distances, higher electrode/electrolyte contact interfaces, and better accommodation of strain upon lithium uptake/release. The significance of nanoscopic architectures has been exemplified in the literature, showing that the idea of developing vanadium-based nanostructures is an exciting prospect to be explored. In this review, we will be casting light on the recent advances in the synthesis of nanostructured vanadium-based cathodes. Furthermore, efficient strategies such as hybridization with foreign matrices and elemental doping are introduced as a possible way to boost their electrochemical performances (e.g., rate capability, cycling stability) to a higher level. Finally, some suggestions relating to the perspectives for the future developments of vanadium-based cathodes are made to provide insight into their commercialization.

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Introduction

The energy industry is in the midst of a transformation since alarm bells started ringing over the environmental pollution caused by the combustion of fossil fuels. As an alternative sustainable energy system, rechargeable lithium ion batteries (LIBs) are leading renewable energy storage technology in the current market. A typical LIB system involves the release of lithium ions from the lithiated cathode and migration across the separator to insert into the anode during charge, and this electrochemical reaction happens in reverse during discharge.^{1–3} Traditional anode materials (e.g., graphite, oxides, and sulfides) generally possess higher theoretical specific capacity compared to cathode materials (e.g., $LiCoO_2$, $LiFePO_4$, and $Li_4Ti_5O_{12}$) and hence a breakthrough in LIBs lies

in the successful research of advanced cathode materials, as this is the primary limiting factor that hinders LIBs from realizing their full potential in terms of energy density. State-of-the-art cathode materials focus on intercalation compounds with a layered or open framework to allow facile Li ion movement. Amongst the cathode materials that share the characteristic of intercalation chemistry, vanadium-based materials, such as V_2O_5 , LiV_3O_8 , $VO_2(B)$ and $Li_3V_2(PO_4)_3$, hold great promise as they possess desirable structures based on arrangements of VO_6 octahedra sharing corners or edges which allow reversible lithium uptake/release, and a number of electrochemically accessible oxidation states (+5, +4, and +3) for electron transition are available. However, progress of these vanadium-based cathodes in commercial applications faces challenges arising from their sluggish lithium ion diffusion and low electrical conductivity.

Nanotechnology is regarded as a means of pushing the frontiers of materials science. With its advances, a new wave of research has been brought about in battery chemistry as the properties of nanomaterials are unattainable at their bulk solid level. It is generally accepted that the transport kinetics of a LIB is governed by the lithium ion diffusion time t , according to the following equation: $t = L^2/D$, where L is the diffusion

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length and D is the diffusion constant.⁴ In other words, the ion and electron transport distance can be tremendously shortened by down-sizing electrode materials to the nano-regime.⁴ Another advantage derived from nanotechnology is that tailored electrode materials are endowed with a higher surface area to allow high lithium-ion flux across the interfaces.⁴ Implementing this concept in vanadium-based cathodes represents a promising way to circumvent the aforementioned problems as nanostructuring offers potential improvements in electrochemical performance by providing shorter mass transport distances, higher electrode/electrolyte contact interfaces, and better accommodation of strain upon lithium uptake/release. The significance of nanoscopic architectures has been exemplified in the literature, showing that the idea of developing vanadium-based nanostructures is an exciting prospect to be explored.^{5–7}

Following previous reviews on some vanadium-based materials in primary lithium batteries^{8,9} and vanadium redox flow batteries,¹⁰ this mini review will summarize some recent developments of vanadium-based (*i.e.*, V_2O_5 , LiV_3O_8 , $VO_2(B)$ and $Li_3V_2(PO_4)_3$ covering the vanadium oxidation states from +5 to +3) nanostructures as cathodes in LIBs (Fig. 1), highlighting crystal structures, electrochemical lithium charge/discharge mechanisms, and the electrode engineering strategies employed in tailoring the phase, morphology, and size based on their classification as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) structures. Furthermore, several approaches such as hybridization and elemental doping will be introduced to explain their contributions towards the enhancement in electrochemical performance of LIBs. Lastly, future prospects for possible

research trends in electrode design and architecture will be discussed.

V_2O_5 nanostructures for LIBs

Orthorhombic V_2O_5 (space group: $Pmmn$; $a = 11.512 \text{ \AA}$, $b = 3.564 \text{ \AA}$, $c = 4.368 \text{ \AA}$) has a layered structural characteristic and its square-pyramidal coordination polyhedron is arranged in an up-up-down-down sequence by sharing edges and corners.¹¹ The intercalation mechanism of Li in V_2O_5 can be generalized as: $V_2O_5 + xLi^+ + xe^- \rightarrow Li_xV_2O_5$, in which a series of phase transitions is associated with the content of inserted Li. Trace amounts of Li intercalation result in α - $Li_xV_2O_5$ ($x < 0.01$) which is subsequently transformed into ϵ - $Li_xV_2O_5$ ($0.35 < x < 0.7$) after further lithiation. Insertion of exactly one Li leads to the formation of δ -phase $Li_xV_2O_5$ but more than that converts it irreversibly to form γ - $Li_xV_2O_5$ ($1 < x < 2$). At maximum Li insertion, irreversible transformation of γ - $Li_xV_2O_5$ to rock-salt type ω - $Li_xV_2O_5$ ($2 < x < 3$) occurs.

Narrowing the particle size of V_2O_5 from the micron- to the nano-scale has made the merits of nanostructuring more prominent. Previous studies synthesizing V_2O_5 nanoparticles have used physical approaches, such as sputtering,^{12,13} thermal evaporation¹⁴ and spray deposition^{15,16} to construct a thin film electrodes. However, nanoparticles have a great tendency to agglomerate and lose their active surface for lithium associated reactions. Thus, great efforts have been made to stabilize them within a foreign matrix or to transform them into a more sustainable structure. For instance, nanocrystalline V_2O_5 nanoparticles have been entrapped in a 3D open framework to exert some kind of confinement on the mobility of the nanoparticles; this will be discussed in the following section. Similar principles have also been employed to substitute the 3D matrix with a microporous filtration membrane.¹⁷ Both these methods minimize a great deal of capacity loss associated with the agglomeration of nanoparticles.

1D V_2O_5 can be categorized into nanorods,^{18,19} nanoribbons,²⁰ and nanowires^{21–23} depending on the different aspect ratio. The electron transport process is much more efficient along the micro-scale axis of 1D V_2O_5 , making it a viable candidate for battery applications. In this regard, V_2O_5 , several centimeters long and 80–120 nm in diameter, was successfully synthesized by Zhai *et al.*²² using a simple hydrothermal method. The as-prepared nanowires exhibit a specific capacity of 175 mA h g^{-1} at a current density of 50 mA g^{-1} during the 20th cycle. A method that combined sol-gel chemistry with electrospinning was developed by Yu and co-workers²³ which enabled the precise control of the dimensions of 1D V_2O_5 without the aid of a sacrificial template. In addition, the annealing process carbonized/evaporated the soft template, rendering the 1-D structure highly porous. This morphological feature facilitates charge transport without destructing the interconnected electron transfer pathway, giving rise to a specific capacity of 370 mA h g^{-1} at 800 mA g^{-1} with a slight capacity fading.

Fig. 1 Some functional vanadium-based nanostructures from 0D nanoparticles to 3D frameworks for LIB applications.

In recent years, 2D materials, including nanosheets^{24,25} and entanglement networks of nanobelts,^{26,27} have been actively pursued as they offer sufficiently high surface areas for electrochemical reaction and their ultrathin thickness is beneficial for enhanced transport kinetics. In a liquid exfoliation method developed by Rui *et al.*,²⁴ small organic molecules (formamide) were used as a delaminating agent to intercalate into the crystal lattice of bulk V_2O_5 . Then, ultrathin V_2O_5 nanosheets can be nicely exfoliated by simple mechanical shaking, as depicted in Fig. 2a. The X-ray diffraction pattern (XRD) shows the successful preparation of the {001} orientated V_2O_5 nanosheets (Fig. 2b). Transmission electron microscopy (TEM) reveals that the V_2O_5 nanosheets have lateral dimensions of 100–400 nm after being dispersed homogeneously in solution for several weeks (Fig. 2c). From the SAED pattern shown in Fig. 2d, highly (001)-oriented diffraction spots can be clearly observed. In addition, atomic force microscopic (AFM)

measurement illustrates that the thickness of a single nanosheet is about 2.1–3.8 nm. The initial charge–discharge voltage profile shows three typical plateaus corresponding to the phase transitions of $\text{V}_2\text{O}_5 \rightarrow \text{Li}_{0.5}\text{V}_2\text{O}_5 \rightarrow \text{Li}_{1.0}\text{V}_2\text{O}_5 \rightarrow \text{Li}_{2.0}\text{V}_2\text{O}_5$ at around 3.4, 3.2 and 2.3 V, respectively. In contrast to the rapid capacity fading of the bulk sample, the nanosheet can still deliver a specific capacity of 274 mA h g^{-1} after 50 cycles, corresponding to 93.8% capacity retention. Moreover, the nanosheets also exhibit an excellent rate performance, in which 2nd-cycle discharge capacities of 266, 251, 233, 192, 156, and 137 mA h g^{-1} can be reached at 1, 3, 5, 10, 20, and 30 C, respectively (Fig. 2e). As illustrated in the Ragone plot (Fig. 2f), the V_2O_5 nanosheet electrode shows impressive high-power and high-energy performance compared to other energy storage devices, with a gravimetric energy of 158 W h kg^{-1} at a power rate of 20 kW kg^{-1} being obtained. The enhanced performance is mainly derived from the unique 2D structure of

Fig. 2 (a) Schematic diagram of the exfoliation of layered bulk V_2O_5 into {001}-oriented few-layered V_2O_5 nanosheets. (b) XRD, (c) TEM image (inset: the digital image of the colloidal acetone dispersion of the V_2O_5 nanosheets), and (d) SAED pattern of the as-prepared V_2O_5 nanosheets. (e) Rate capability of the V_2O_5 nanosheets and bulk V_2O_5 between 4.0 and 2.05 V. (f) The Ragone plot of V_2O_5 nanosheets, in comparison with some advanced energy storage and conversion systems. Reproduced with permission from ref. 24. Copyright 2012, Royal Society of Chemistry.

Fig. 3 (a–b) FESEM images; (c–e) TEM images of the HVO nanobelts. The inset in (c) is a magnified view to show the width of the nanobelts. (d) Side view of a rolled up nanobelt to show a thickness of about 10 nm. (e) HRTEM image of an individual nanobelt with its corresponding SAED pattern (inset). (f) Optical image of a freestanding HVO bulky paper based on an intertwining network of the above HVO nanobelts without the addition of any binder. Reproduced with permission from ref. 26. Copyright 2011, Royal Society of Chemistry.

V_2O_5 , giving a higher surface area, shorter diffusion paths for charge carriers and better strain relaxation upon lithium intercalation/de-intercalation.

On the other hand, the concept of using an entanglement network of 1D V_2O_5 as a binder-free electrode was practically illustrated by Rui and co-workers.²⁶ Hydrated V_2O_5 (HVO) nanobelts were synthesized *via* a hydrothermal method. The microscopy images of the HVO show that the HVO possesses nanobelt morphology with lengths of 100–400 nm (Fig. 3a and b), widths of 20–600 nm (Fig. 3c), and thicknesses of 10 nm (Fig. 3d). As depicted in Fig. 3e, the HVO nanobelts are highly crystalline with the long micron-axis being orientated along the [010] direction. Successful attempts to fabricate the HVO into bulky paper have been demonstrated in Fig. 3f, in which the flexible electrode is robust upon bending. The absence of a polymeric binder (*e.g.*, PVDF) neither disrupts the electrode integrity nor its flexibility. The electrochemical charge and discharge tests reveal that the HVO bulky paper electrode could still consistently maintain almost 100% Coulombic efficiency during 20 cycles despite a slight drop in discharge capacity. Moreover, the electrode can deliver discharge capacities of 283, 241, 212, 194, 183, and 163 mA h g^{-1} during the 2nd cycle at current rates of 0.34, 0.68, 1.7, 2.7, 3.4 and 6.8 C, respectively, which outperforms traditional PVDF-added HVO cathodes. Electrochemical impedance measurements demonstrate the benefit of excluding the electro-inert binder; the smaller radius of the semi-circle of the binder-free HVO electrode clearly indicates its lower charge transfer resistance compared to PVDF-added HVO cathodes. The enhance-

ment is closely associated with the intertwined nanobelt network that provides hierarchical porous channels for better ion penetration and with the binder-free fabrication that improves the electronic conductivity.

A 3D robust framework is adopted to enable free penetration of ions, allowing every single active site to be easily accessible. Furthermore, an interconnected framework also constructs a continuous highway for better electron transport. Furthermore, the construction of secondary structures that are self-assembled from nanoparticles in a polyol-mediated environment, in particular hollow spheres, have been shown to be able to allow excellent charge transport while being able to prevent nanoparticles from aggregating into large clusters. In a previous study, V_2O_5 thin films composed of an interconnected porous network were successfully synthesized using a simple electrostatic spray pyrolysis method.²⁸ Its excellent rate performance is derived from the porous framework which enables fast lithium diffusion, giving rise to it retaining a specific capacity of 87 mA h g^{-1} at 56 C (8232 mA g^{-1}). Additionally, nanoscale V_2O_5 building blocks with different morphologies have also been strategically assembled into 3D structures.^{29–31} For instance, Pan *et al.*²⁹ developed a facile solvothermal method to obtain hierarchical V_2O_5 hollow microflowers. The as-prepared sample exhibits good capacity retention in the cycling test, showing a capacity loss of only 0.27% in each cycle in a voltage window of 2.0–4.0 V.

The presence of a graphitic support proved to be essential in addressing the electronic conductivity and structural stability of V_2O_5 and the carbonaceous materials can be categorized

Fig. 4 (a) Schematic illustration of the evolution of porous V_2O_5 spheres on the surface of rGO sheets. (b) SEM image of the rVO/rGO sample before undergoing annealing. (c–e) SEM images of the $\text{V}_2\text{O}_5/\text{rGO}$ (46 wt%) sample after annealing, showing that these V_2O_5 spheres are highly porous. (f) Charge/discharge capacities at various current densities from 190 to 5700 mA g^{-1} . (g) Cycling performance at a high current density of 5700 mA g^{-1} . Reproduced with permission from ref. 39. Copyright 2011, Royal Society of Chemistry.

into 1D CNTs,^{32–35} 2D graphenes,^{36–38} *etc.* In this regard, Rui *et al.*³⁹ hybridized reduced graphene oxide (rGO) with highly porous V_2O_5 spheres (denoted as $\text{V}_2\text{O}_5/\text{rGO}$) using a simple solvothermal method, as shown in Fig. 4a. Uniform attachment of rGO onto the surface of the V_2O_5 spheres is driven by the heterogeneous nucleation and precipitation of vanadium on rGO before sintering. After the annealing process, the V_2O_5 nanoparticles tend to assemble into hollow spheres to reduce the total surface energy. Before sintering, V_2O_5 with particle sizes of 10–50 nm are uniformly attached onto the surface of rGO (Fig. 4b). Interestingly, they turn into hollow spheres with

diameters of 200–800 nm (Fig. 4c and d) and are constructed from interconnected small grains of 50 nm (Fig. 4e). The weight percentage of rGO is about 46 wt%. Such a hybrid exhibits a relatively low capacity fading rate of 90 mA g^{-1} , in which about 0.30% of capacity is lost per cycle over a total of 50 cycles. Rate performance testing displays 211, 200, 184, 175, 167, 127 and 102 mA h g^{-1} during the 2nd cycle at 190 (0.65 C), 380 (1.3 C), 950 (3.2 C), 1520 (5.2 C), 1900 (6.5 C), 3800 (13 C) and 5700 mA g^{-1} (19 C), respectively (Fig. 4f). In addition, even at a current density as high as 5700 mA g^{-1} (19 C), the electrode can still achieve 93 mA h g^{-1} after 200 cycles (Fig. 4g). These enhancements can be explained by the conductive support and the unique hollow structure. The presence of rGO facilitates the charge transfer between the active materials and the current collector. In addition, the porous and hollow architecture provides a shorter lithium diffusion path by giving better electrolyte penetration to the active materials.

Doping of V_2O_5 has been introduced to replace V with other cations (Ag^+ , Cu^{2+} , Cr^{3+} , Mn^{2+} , Sn^{2+} , *etc.*)^{40–44} to alter the valence state of V for high electronic conductivity and better lithium ion diffusion across the crystal lattice of V_2O_5 . Yu *et al.*⁴¹ synthesized hierarchical Cu-doped V_2O_5 (*e.g.*, $\text{Cu}_{0.02}\text{V}_{1.98}\text{O}_5$) flowers that self-assembled from V_2O_5 nanobelts using a simple hydrothermal method. The formation mechanism of the Cu-doped V_2O_5 , shown in Fig. 5a, begins with the preferential growth of nanoparticles into nanobelts followed by the self-assembly of flower-like secondary structures without any aid from a surfactant. From the SEM images, the $10 \mu\text{m}$ flower-like porous network (Fig. 5b) is constructed from nanobelts with a lateral dimension of $\sim 100 \text{ nm}$ (Fig. 5c). It is also found that the Cu-doped V_2O_5 nanobelts are highly crystalline with a long axis along the [010] direction (Fig. 5d and e). Comparing the CV curves of pure V_2O_5 (Fig. 5f) and the Cu-doped V_2O_5 nanobelts (Fig. 5g), the doped sample shows better symmetry. Explanation of such an observation is that the structural changes are suppressed after Cu doping, giving rise to better reversibility and stability. In addition, the electrochemical performance of the Cu-doped V_2O_5 surpasses the un-doped sample. For example, the cycling retentions of the Cu-doped V_2O_5 ($\text{V}_2\text{O}_5\cdot 2$, $\text{Cu}_{0.02}\text{V}_{1.98}\text{O}_5$) and the un-doped samples are 85% and 69%, respectively during the 50th cycle (Fig. 5h). The Cu-doped V_2O_5 also shows promising results in rate performance, in which 2nd cycle capacities of 229, 197, 182, 126 and 97 mA h g^{-1} can be achieved at 1.0, 3.0, 5.0, 10.0 and 20.0 C, respectively (Fig. 5i). The authors attributed this to the Cu-doping decreasing the charge transfer resistance by improving the lithium diffusion kinetics of the Faradic reactions, giving rise to a better cycling performance and rate capability.

Furthermore, the structural characteristics of V_2O_5 enable the intercalation of cations or small molecules (other than Li) at the interlayer positions between square pyramidal VO_5 layers.^{45–47} Such an interesting property has inspired researchers to tune the lithium ion diffusion rate and collapse of the lattice structure by modifying the interlayer spacing of V_2O_5 .

Fig. 5 (a) Schematic illustration of the evolution of nanobelt-assembled flowers from nanoparticles. (b) SEM image, (c) TEM image (d) HRTEM image and (e) SAED pattern of the post-annealed V₂O₅-2 (*i.e.*, Cu_{0.02}V_{1.98}O₅) sample. CV curves of (f) V₂O₅-0 (pure V₂O₅) and (g) V₂O₅-2 samples during the second cycle at a scan rate of 0.2 mV s⁻¹. (h) Cycling performance of three electrodes for the first 50 cycles at a current density of 58.8 mA g⁻¹ (0.2 C). V₂O₅-1 is Cu_{0.01}V_{1.99}O₅. (i) Rate capability at various current densities from 1.0 to 20.0 C. Reproduced with permission from ref. 41. Copyright 2013, Royal Society of Chemistry.

A previous study made a successful attempt to control the hydration level and sodium content of Na_xV₂O₅·*n*H₂O using a chimie douce strategy.⁴⁵ Electrochemical assessment of the hydrated sodium vanadium oxides reveals that the capacities increase with decreasing water content, with specific capacities of 170 and 300 mA h g⁻¹ being achieved by Na_{0.12}V₂O₅·0.23H₂O and Na_{0.32}V₂O₅·0.01H₂O, respectively, at a discharge rate of C/20.

LiV₃O₈ nanostructures for LIBs

Layered trivanadate, LiV₃O₈ belongs to a monoclinic system (space group: *P*2₁/*m*, *a* = 6.680 Å, *b* = 3.596 Å, *c* = 12.024 Å), in which the immobile Li⁺ ions reside in the octahedral coordination site of the [V₃O₈] interlayer space.⁴⁸ It is interesting that the empty tetrahedral sites of LiV₃O₈ can be continuously occupied by incoming Li⁺ ions during discharge without causing irreversible distortion of the crystal structure, leading to the formation of non-stoichiometric Li_{1+x}V₃O₈ (0 < *x* < 3) that is able to accommodate up to 3 Li⁺ per formula unit and has a theoretical capacity of 280 mA h g⁻¹.⁴⁹

The lithium insertion process of Li_{1+x}V₃O₈ involves several phase transition steps. Single-phase transitions occur at potentials of 3.5, 2.8, 2.7, and 2.3–2.4 V, in which Li⁺ fills the tetrahedral sites. Furthermore, Li⁺ fills the octahedral sites (Li₃V₃O₈ to Li₄V₃O₈) *via* a two-phase transition at a potential of 2.5 V.^{50–53} At a relatively low potential of 2.3 V, the slow kinetic intercalation step is regarded as the origin of capacity fading due to reactions between the Li₄V₃O₈ and the electrolyte that

lead to passive film formation or dissolution of the active species.⁵⁴

To have more precise control over the homogeneity and particle size of LiV₃O₈, solid-state reactions and traditional high-temperature sintering methods have been substituted with alternative approaches, such as sol-gel methods,^{51,55–57} hydrothermal reactions,^{58,59} microwave-assisted reactions,^{60,61} spray pyrolysis,⁶² and topotactic synthesis,⁶³ *etc.* Xu *et al.*⁶³ topotactically synthesized ultralong LiV₃O₈ nanowires from a H₂V₃O₈ precursor. The lithium substitution process is allowed owing to the similarity of their layered crystal structures. Fig. 6a–c show the morphology and microstructure of the as-synthesized LiV₃O₈. The 1D morphology is retained after calcination at 450 °C. Fig. 6d depicts the characteristic redox peaks of LiV₃O₈ in the voltage range 4.0–1.5 V, which is in accordance with the charge/discharge curves shown in Fig. 6e. It is found that the LiV₃O₈ electrode calcined at 450 °C achieves the best performances in rate capability and cycling tests. As demonstrated in Fig. 6f, discharge capacities of 279, 269, 253, 237, 222, 211 and 196 mA h g⁻¹ at current densities of 50, 100, 200, 300, 400, 500 and 600 mA g⁻¹, respectively, are achieved by the LiV₃O₈ electrode calcined at 450 °C. Moreover, it also performs well at high current densities, in which discharge capacities of 160 and 120 mA h g⁻¹ are retained after 400 and 600 cycles, respectively.

Other than tuning the particle size and morphology of LiV₃O₈, several approaches have been devised to improve the electrochemical performance of LiV₃O₈ by controlling its crystallinity,^{64,65} tailoring the interlayer spacing,^{59,66} cation substitution,^{67–69} doping,^{70,71} and surface coating.^{72,73} The influence of the degree of crystallinity on the performance of

Fig. 6 (a and b) SEM images of the precursor $\text{H}_2\text{V}_3\text{O}_8$ nanowires and the LiV_3O_8 nanowires calcined at 450°C , respectively. (c) TEM image and SAED pattern (inset) of the LiV_3O_8 nanowires prepared at 450°C . (d) Cyclic voltammetry curves at a scan rate of 0.1 mV s^{-1} in the potential range 4.0 to 1.5 V vs. Li^+/Li . (e) The initial charge-discharge curves at a current density of 20 mA g^{-1} . (f) Discharge capacities of the LiV_3O_8 nanowire cathode at various current densities. (g) Charge-discharge cycling test of the LiV_3O_8 nanowire cathode at current densities of 1500 and 2000 mA g^{-1} . Reproduced with permission from ref. 63. Copyright 2012, Nature.

LiV_3O_8 is still a controversial issue. Early reports showed that the better electrochemical performances of low crystallinity LiV_3O_8 were due to the fact that the presence of bound water molecules enlarged the lattice spacing of LiV_3O_8 , increasing the mobility of Li^+ ions across the 2D diffusion pathway.^{64,65} However, a later study reported by Pan *et al.*,⁵¹ proved that the disordered atom arrangement of low crystallinity LiV_3O_8 may interfere with Li^+ ion diffusion across the host material. Applying the similar concept of the previous report that controlled the crystallinity of LiV_3O_8 to increase the interlayer spacing, Yu *et al.*⁶⁶ synthesized LiV_3O_8 and deliberately intercalated water molecules into its host lattice. The hydrated LiV_3O_8 (250 mA h g^{-1}) delivers a higher specific capacity than crystalline or dehydrated LiV_3O_8 (175 mA h g^{-1}) and shows better cycling stability. Cation substitution has been employed to improve the crystal lattice stability during the rearrangement of oxygen packing upon phase transition. For example, Ni-doping improves the cycling stability of pristine LiV_3O_8 . A specific capacity of 251 mA h g^{-1} is retained after 30 cycles at 0.5 C by the Ni doped LiV_3O_8 , surpassing that of the undoped sample.

$\text{VO}_2(\text{B})$ nanostructures for LIBs

VO_2 exists in several polymorphic forms, such as rutile $\text{VO}_2(\text{R})$, monoclinically distorted rutile $\text{VO}_2(\text{M})$, tetragonal $\text{VO}_2(\text{A})$, and monoclinic $\text{VO}_2(\text{B})$.⁷⁴ In particular, the metastable $\text{VO}_2(\text{B})$ has a layered structural characteristic, in which adjacent VO_5 square pyramids are connected at their basal edges with the vanadyl groups arranging in an alternate up and down

manner.⁷⁵ Typical plateaus observed at 2.5 V during discharge and at 2.6 V during charge in the CV measurement represent the reversible insertion and withdrawal of lithium into the layered structure of $\text{VO}_2(\text{B})$, giving rise to a theoretical capacity of 161 mA h g^{-1} . Its general expression is shown as follows:⁷⁶

Nanocrystalline $\text{VO}_2(\text{B})$ has been documented to be synthesized by reduction of V_2O_5 powder using borohydride solution.^{77,78} By using this method, the particle size of $\text{VO}_2(\text{B})$ can be reduced to approximately 100 nm . In the literature, $\text{VO}_2(\text{B})$ has been mostly reported as 1D nanostructures.^{74,78–80} Although good lithium storage properties have been attained using 1D nanostructures, their rate capabilities are still far from being satisfactory. Hence, carbon coating^{81–83} and hybridizing with carbonaceous materials^{83–88} have been implemented to improve the electronic conductivity of $\text{VO}_2(\text{B})$. In this regard, carbon coated $\text{VO}_2(\text{B})$ was synthesized by Rui *et al.*⁸¹ using a hydrothermal method, in which the *in situ* growth of amorphous carbon derived from sucrose is closely attached onto the surface of $\text{VO}_2(\text{B})$. The belt-like morphology of the $\text{VO}_2(\text{B})@\text{C}(6.6\text{ wt}\%)$ sample is shown in Fig. 7a, and possesses a width of $\sim 120\text{--}130\text{ nm}$ (Fig. 7b) and a thickness of $\sim 25\text{ nm}$ (Fig. 7c). From the HRTEM image shown in Fig. 7d, the thickness of the amorphous carbon layer is approximately 4.3 nm . The thickness of the carbon layer is controllable by adjusting the concentration of sucrose. Having a relatively thick carbon layer may block the lithium diffusion pathway, although the electrical conductivity and the structural strain accommodation can be improved substantially. Hence, only an

Fig. 7 (a–c) FESEM images and (d) HRTEM image of the $\text{VO}_2(\text{B})@\text{C}$ nanobelts. (e–g) Cathode performance of the $\text{VO}_2(\text{B})@\text{C}$ nanobelts in the voltage range 4.0–2.0 V. (e) Initial galvanostatic charge–discharge voltage profiles at a current density of 100 mA g^{-1} . (f) Cycling performance at a current density of 100 mA g^{-1} . (g) Discharge capacities of $\text{VO}_2(\text{B})@\text{C}$ electrodes at various current densities. Reproduced with permission from ref. 81. Copyright 2011, Royal Society of Chemistry.

optimum thickness of carbon layer renders the electrode with an excellent electrochemical performance. The voltage profiles (Fig. 7e) and cycling performances (Fig. 7f) of the $\text{VO}_2(\text{B})@\text{C}$ samples are similar. However, the $\text{VO}_2(\text{B})@\text{C}(6.6 \text{ wt}\%)$ exhibits the best rate capability, in which discharge capacities of 157, 155, 146 and 136 mA h g^{-1} can be achieved during the 2nd cycle at current densities of 200 (1.2 C), 500 (3.1 C), 800 (5.0 C) and 1000 mA g^{-1} (6.2 C), respectively, by striking a balance between the electronic conductivity and lithium ion diffusion efficiency (Fig. 7g). As revealed by electrochemical impedance spectrum (EIS) measurements, the $\text{VO}_2(\text{B})@\text{C}(6.6 \text{ wt}\%)$ cathode shows a semi-circle with the smallest radius amongst the other samples, indicating its faster kinetics for the Faradic reactions by having the lowest charge-transfer resistance.

As an alternative to further improve the electrochemical performance, studies have been carried out to incorporate functional nanostructures to mitigate the structural stability problem during lithiation/de-lithiation. In particular, Mai and co-workers⁸⁹ successfully demonstrated the idea of using nanoscroll-buffered hybrid nanostructured VO_2 composed of nanobelts and nanowires using a hydrothermally-driven splitting and self-rolled method. The unique structural features of the buffer layer offer facile relaxation strain to accommodate the volume variation during electrochemical reaction, enabling it to retain 82% of its initial capacity after 1000 cycles at 9 C (1000 mA g^{-1}). Substantial efforts have been dedicated to the

synthesis of $\text{VO}_2(\text{B})$ in 3D nanostructures, including sacrificial-template or template-free approaches.^{90–92} It is believed that radially-protruding $\text{VO}_2(\text{B})$ nanostructures that assemble into a sphere have better accommodation to expansion/shrinkage and are able to suppress self-aggregation.

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ nanostructures for LIBs

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) exists in two different polymorphic forms which are rhombohedral (or so-called NASICON) and monoclinic phases. The NASICON framework of LVP (space group: $R\bar{3}c$; $a = 8.316 \text{ \AA}$, and $c = 22.484 \text{ \AA}$) is constructed from VO_6 octahedra and PO_4 tetrahedra interconnected through their vertices in the [001] direction to form the $[\text{V}_2(\text{PO}_4)_3]$ lantern, where the lithium is located in a 4-fold coordinated interstitial site.⁹³ Compared to rhombohedral LVP, monoclinic LVP (space group: $P2_1/n$, $a = 8.605 \text{ \AA}$, $b = 8.591 \text{ \AA}$, $c = 12.038 \text{ \AA}$, and $\beta = 90.600^\circ$) is more thermodynamically stable. Its VO_6 octahedra and PO_4 tetrahedra are connected through oxygen vertices, where three crystallographic interstitial voids are available for the occupancy of lithium.⁹⁴

Their structural differences result in distinct electrochemical reactions. Rhombohedral LVP is reported to undergo a two-phase transition between the compositions of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{LiV}_2(\text{PO}_4)_3$ (3.7 V), involving a $\text{V}^{3+}/\text{V}^{4+}$ redox couple. The sym-

metry of monoclinic LVP allows three lithium ions that are accommodated within the $[V_2(PO_4)_3]$ lanterns to be mobile enough to participate in electrochemical reactions (in the voltage range of 3.0–4.8 V). During the de-lithiation step, the lithium content of $Li_xV_2(PO_4)_3$ varies from $x = 3.0, 2.5, 2.0, 1.0$ and 0 through a complex series of phase transitions, corresponding to the following equations:

The working potential of LVP is relatively higher than other vanadium-based cathodes, as 3 lithium de-intercalation reactions within a voltage range of 3.0–4.8 V are achievable, giving rise to a theoretical capacity of 197 mA h g^{-1} . A systematic study by Rui and co-workers⁹⁵ found that the correlation between the voltage state of the charge/discharge and the chemical diffusion coefficient of lithium ions in LVP in the potential range of 3.0–4.8 V did not change significantly in spite of using different techniques (CV, GITT, and EIS). As illustrated in Fig. 8, all these three measurements show a “W” shape curve which is indicative of the characteristics of insertion-host materials. Furthermore, the chemical diffusion coefficients derived from the aforementioned techniques are in the range of 10^{-19} – $10^{-10} \text{ cm}^2 \text{ s}^{-1}$, indicating that LVP is a promising candidate for high-rate battery applications.

In the literature, significant improvements have been observed when LVP bulk materials are engineered to reach the nano-level. The most commonly used methods are traditional solid-state reactions,^{96–98} sol-gel reactions,^{99–101} hydrothermal

methods,^{102–104} spray pyrolysis, and other methods.^{105–107} Compared to the aforementioned methods, sol-gel and hydrothermal reactions are more favorable as they can produce LVP nanoparticles with good homogeneity, uniform morphology and controllable particle size, giving rise to a higher charge/discharge rate. For instance, Liu *et al.*¹⁰⁴ reported that uniform LVP nanorods with a diameter of $\sim 60 \text{ nm}$ and a length of 0.5 – $1.0 \text{ }\mu\text{m}$ can be synthesized using a hydrothermal method. The LVP nanorods show good rate performance, and specific capacities of $141.6, 136.1, 134.6, 124.8$ and $101.1 \text{ mA h g}^{-1}$ can be delivered at $0.5, 1, 2, 5$ and 10 C , respectively, in the voltage range of 3.0 – 4.6 V . LVP with particle sizes in the range 200 – 500 nm have also been successfully synthesized using a sol-gel method.¹⁰⁸ It shows a specific capacity of about 100 mA h g^{-1} at 1 C after 80 cycles and close to 100% Coulombic efficiency during the cycling test. To meet the burgeoning demand for cathode materials with good performance, LVP nanomaterials have been further modified to overcome their kinetic limitations. Several approaches will be covered in this review: (1) carbon coating;^{109–111} (2) other additive coating;^{112–114} and (3) doping. Carbonaceous materials (graphene and amorphous carbon) and conductive additives (Ag, Nb, glassy lithium phosphate, SiO_2) are coated onto the surface of LVP for the same reason that conductive matrices and buffer layers were used above: to restrain structural deformation. Non-conductive additives (MgO and SiO_2) are used to stabilize the structure of LVP to reduce dissolution and decrease the interface charge transfer resistance. The doping system is complicated, and dopants can be supervalent cations ($\text{Na}^+, \text{Ca}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}, \text{Mg}^{2+}, \text{Fe}^{3+}$, *etc.*),^{115–120} and anions (F^- and Cl^-).^{121,122} It is found that this approach can improve the intrinsic electronic conductivity and lithium ion diffusion of LVP.

In an interesting report, the influences of different carbon sources on the electrochemical performances of LVP electrodes were investigated.¹⁰⁹ Here, micron-size LVP were synthesized by a carbon thermal reduction process using citric acid, glucose, PVDF and starch as both reducing agents and carbon coating sources. The four as-prepared samples show good rate capability and display almost no capacity fading after 100 cycles in the voltage range 3.0 – 4.3 V . These good performances could be attributed to the presence of a uniform carbon layer which reduces the resistance and improves the electronic conductivity. Furthermore, Rui *et al.*¹¹⁰ demonstrated the possibility of coupling ultrafine LVP embedded in a nanoporous carbon matrix with reduced graphene oxide (rGO), so-called LVP-NC@NPCM@rGO, to build a binder-free cathode for LIBs. LVP-NC@NPCM@rGO was synthesized using sol-gel chemistry followed by a thermal annealing process. 20 – 80 nm quasi-spherical nanoparticles are uniformly attached on the surface of the rGO and nanocrystals with sizes of 5 – 8 nm are embedded in a single cluster. LVP-NC@NPCM@rGO shows excellent rate capability, with discharge capacities of $168, 164, 160, 154, 145, 136, 126$ and 109 mA h g^{-1} being achieved during the 2nd cycle at current densities of $197 (1 \text{ C}), 394 (2 \text{ C}), 591 (3 \text{ C}), 985 (5 \text{ C}), 1970 (10 \text{ C}), 2955 (15 \text{ C}), 3940 (20 \text{ C})$ and

Fig. 8 Comparison of the chemical diffusion coefficients of LVP as determined by CV, GITT, and EIS. Reproduced with permission from ref. 95. Copyright 2010, Elsevier.

5910 mA g⁻¹ (30 °C), respectively, between 3.0 and 4.3 V. Impressively, in the wider voltage window of 3.0–4.8 V, LVP-NC@NPCM@rGO can still exhibit a superior high-C-rate performance, *e.g.*, 109 mA h g⁻¹ at 5910 mA g⁻¹ (30 °C), and even a delivers specific capacity of 91 mA h g⁻¹ after cycling for 1000 cycles at 30 °C. Besides the contribution of nano-sizing, the electrochemical improvement of LVP-NC@NPCM@rGO can be attributed to the following aspects: (1) the nanoporous carbon matrix facilitates fast Li⁺ and e⁻ transport across the active material/electrolyte interfaces and cushions the structural deformation of the LVP nanocrystals; (2) the highly conductive rGO network enables better charge transfer between the active materials and the current collector; (3) binder-free fabrication avoids electro-inert species and allows better electrolyte permeation.

Conclusions and perspectives

In summary, this mini review highlights recent advances in the design and fabrication of nanostructured vanadium-based electrodes (*i.e.*, V₂O₅, VO₂(B), Li₃V₂(PO₄)₃ and LiV₃O₈) for LIB applications. It is found that the intrinsic disadvantages of vanadium-based cathodes have been alleviated by exploiting their newly emerging properties that are tailored by nanostructuring. Furthermore, the concepts of hybridization with foreign matrices (conductive and non-conductive substrates such as carbonaceous materials, metals, and metal oxides) and elemental doping have brought about further improvement of existing single-phase vanadium-based cathodes. Additionally, significant advances have also been achieved in electrode fabrication processes, making electrodes more flexible, efficient, and accessible to electrolyte.

Although the aforementioned concepts have experimentally demonstrated their feasibility to be electrochemically lithiated/delithiated, there large challenges still remain to directly put them into practice. So far, almost all methodologies for the fabrication of nanoarchitected vanadium-based electrodes are still stuck at the laboratory scale and are far from meeting the specifications of industrial standards. Synthesis of desired vanadium-based nanoarchitectures with a high capacity and a high rate performance is a significant step towards practical applications. Another concern is that vanadium oxides and some salts of vanadium have moderate toxicity. Furthermore, despite nanostructures with high surface-to-volume ratios, which can facilitate efficient Li⁺ transfer between the electrolyte and the active materials to achieve high-power performances, irreversible capacity caused by the formation of passivation layers, or uncontrolled reactions, are greater problems. Regarding vanadium oxide cathodes, it is easy to form some irreversible lithiated phases when they are deeply discharged, which will result in serious capacity fading. In addition, vanadium oxide cathodes (*e.g.*, V₂O₅ and VO₂(B)) are Li deficient and may only be suitable for non-rechargeable primary lithium batteries in practice.

Applications of nanostructured vanadium-based cathode materials in LIB technology are still at the stage of research and development. To realize a wide range of industrial applications, further work is required to achieve progress on green and large-scale production, LIB performances and electrochemical characteristics, design of new vanadium-based cathodes, and so on. Synthetic processes of vanadium-based cathodes have to fulfil several requirements, such as being simple, scalable for mass production, cheap, and environmentally benign to have any prospect in commercial applications. Hence, there is still room for improvement and optimization of synthetic protocols to achieve this goal. Continuous improvement in cycling stability and rate capability of vanadium-based cathodes with nanocrystallization, surface coating, element substitution, material processing, *etc.*, is needed. For example, there is still great development space to tailor the nanoarchitectures and morphologies to obtain more favourable lithium storage properties, and a promising direction is the introduction of more complex hierarchical 3D micro-/nanostructures with internal voids/pore space, which can avoid some limitations of using simple one component nanostructures. Furthermore, it is also highly essential to study the fundamental issues associated with the electrochemical characteristics (*e.g.*, the kinetics of electron/ion transport at the electrode/electrolyte interface) of nanostructured vanadium-based cathodes, which is regarded as a key for further breakthroughs in materials optimization. Furthermore, searching for new vanadium-based cathodes with special characteristics (*e.g.*, a stable crystal structure, high electrical conductivity, high working potential, *etc.*) is also expected to significantly enhance their practical use in LIB devices.

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