Boosting the Rate and Cycling Performance of β -Li_xV₂O₅ Nanorods for Li Ion Battery by Electrode Surface Decoration

Panpan Wang, Yue Du, Baoyou Zhang, Yanxin Yao, Yuchen Xiao, Lijie Ci, Chengyan Xu, Liang Zhen

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The β -phase lithium vanadium oxide bronze (β -Li_xV₂O₅) with high theoretic specific capacity up to 440 mAh g⁻¹ is considered as promising cathode materials, however, their practical application is hindered by its poor ionic and electronic conductivity, resulting in unsatisfied cyclic stability and rate capability. Herein, we report the surface decoration of β -Li_xV₂O₅ cathode using both reduced oxide graphene and ionic conductor LaPO₄, which significantly promotes the electronic transfer and Li⁺ diffusion rate, respectively. As a result, the rGO/LaPO₄/Li_xV₂O₅ composite exhibits excellent electrochemical performance in terms of high reversible specific capacity of 275.7 mAh g⁻¹ with high capacity retention of 84.1% after 100 cycles at a current density of 60 mA g⁻¹, and acceptable specific capacity of 170.3 mAh g⁻¹ at high current density of 400 mA g⁻¹. The cycled electrode is also analyzed by electrochemical impedance spectroscopy, ex-situ X-ray diffraction and scanning electron microscope, providing further insights into the improvement of electrochemical performance. Our results provide an effective approach to boost the electrochemical properties of lithium vanadates for practical application in lithium ion batteries.

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Boosting the rate and cycling performance of $\beta\text{-Li}_x\text{V}_2\text{O}_5$ nanorods for Li ion battery by electrode surface decoration

Pan-Pan Wang^{a,b,c}, Yue Du^{a,c}, Bao-You Zhang^b, Yan-Xin Yao^b, Yu-Chen Xiao^b, Li-Jie Ci^a, Cheng-Yan Xu^{a,b,c,*}, Liang Zhen^{a,b,c,*}

^a School of Materials Science and Engineering, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China

^b School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

^c MOE Key Laboratory of Micro-Systems and Micro-Structures Manufacturing, Harbin Institute of Technology, Harbin 150080, China

E-mail: lzhen@hit.edu.cn (L.Z.); cy_xu@hit.edu.cn (C.Y.X.)

Abstract: The β -phase lithium vanadium oxide bronze ($\beta\text{-Li}_x\text{V}_2\text{O}_5$) with high theoretic specific capacity up to 440 mAh g⁻¹ is considered as promising cathode materials, however, their practical application is hindered by its poor ionic and electronic conductivity, resulting in unsatisfied cyclic stability and rate capability. Herein, we report the surface decoration of $\beta\text{-Li}_x\text{V}_2\text{O}_5$ cathode using both reduced oxide graphene and ionic conductor LaPO₄, which significantly promotes the electronic transfer and Li⁺ diffusion rate, respectively. As a result, the rGO/LaPO₄/Li_xV₂O₅ composite exhibits excellent electrochemical performance in terms of high reversible specific capacity of 275.7 mAh g⁻¹ with high capacity retention of 84.1% after 100 cycles at a current density of 60 mA g⁻¹, and acceptable specific capacity of 170.3 mAh g⁻¹ at high current density of 400 mA g⁻¹. The cycled

electrode is also analyzed by electrochemical impedance spectroscopy, *ex-situ* X-ray diffraction and scanning electron microscope, providing further insights into the improvement of electrochemical performance. Our results provide an effective approach to boost the electrochemical properties of lithium vanadates for practical application in lithium ion batteries.

Keywords: β - $\text{Li}_x\text{V}_2\text{O}_5$, cyclic stability, reduced oxide graphene, ionic conductor, surface decoration

1. Introduction

Due to the attractive merits of high energy density, long cyclic life and environmental friendliness, rechargeable lithium ion batteries (LIBs) have been widely used as power source for portable electronic devices.[1-3] Despite that, the energy and power density of current commercial LIBs was still far from satisfying the urgent requirements for further applications in electric vehicles and smart grids. The limited capacity of commonly used cathodes, including LiCoO_2 , LiFePO_4 , LiMn_2O_4 and Li-excess layered oxide compounds, is the main limiting factor for the realization of high energy-density LIBs, which delivered lower reversible capacities ($<280 \text{ mAh g}^{-1}$) than the counterpart graphite anode. To this end, cathode material with higher specific capacity are urgently needed to meet the ever-increasing goals for high energy-density LIBs. [4, 5]

Recently, vanadium oxides and their derivatives have received tremendous attention due to their rich chemistry and high specific capacity as LIBs cathode. [6-8] As for V_2O_5 , its theoretical capacity reaches up to 440 mAh g^{-1} because

more than 3 lithium ions per formula can be inserted into V_2O_5 layer, whereas the capacity of V_2O_5 cathode decays seriously after initial cycling due to the irreversible phase transformation and local structure collapse when the lithium uptakes more than 2 moles per formula unit.[9, 10] Different from layered V_2O_5 , β -phase vanadium oxide bronzes (β - $M_xV_2O_5$, M = alkali, alkaline earth, and transition metals) adopts more stable and rigid crystal structures with the $[VO_6]$ octahedrons layers pillared by $[VO_5]$ square pyramids.[11] The unique 3D framework contained several feasible interstitial sites in the tunnel structure, endowing the vanadium oxide bronzes rather good structural reversibility upon large amount of lithium accommodation, while maintaining high capacity features. [12-15] Despite these advantages, one major drawback of pure β -phase vanadate cathode is its inferior rate capability and cycling stability,[16, 17] which was believed to be related with its intrinsic poor electronic conductivity and relatively slow Li^+ diffusion kinetic, especially upon deep lithiation. Meanwhile, the fragile interfacial property of pristine vanadate electrode with the risk of erosion from the electrolytes and vanadium dissolution is considered to be another reason for capacity fading.[18] Thus, modification strategies are imperative to overcome these limitations, thereby boosting the electrochemical properties of lithium vanadate cathode.[19]

Surface modification with conducting materials (e.g., graphene,[20, 21] polymer,[22, 23]) or ionic conductors (phosphates,[24] metal oxides,[25, 26] etc.) is proved to be efficient to enhance the electrochemical properties of

vanadate oxide cathode. Recently, two-dimensional graphene-based materials were emerging as an eye-catching coating candidate with superior electrical conductivity, which was usually hybrid with active materials through hydrothermal route or calcination treatment in reductive atmosphere. Whereas the coexisted V^{4+} and V^{5+} in $\beta\text{-Li}_x\text{V}_2\text{O}_5$ are susceptible to the reductive graphene during the hybridization process especially under high calcination temperature, resulting in undesired impurity phase or even inducing irreversible phase transition and thus capacity loss of the cathode. To achieve a uniform graphene coating layer on $\beta\text{-Li}_x\text{V}_2\text{O}_5$ with complex valence states while maintain the $\beta\text{-Li}_x\text{V}_2\text{O}_5$ phase is still a big challenge. Herein, a gentle freeze drying strategy with ionic conductor decoration was applied successfully to tackle these issues.

In this work, the conductive reduced oxide graphene (rGO) and ionic conductor LaPO_4 were employed to engineer the interfacial chemistry of $\beta\text{-Li}_x\text{V}_2\text{O}_5$ cathode via chemical precipitation route followed by frozen dryness. The obtained rGO/ LaPO_4 /LVO electrode demonstrated remarkable cycling stability and superior rate capability with specific Li^+ multiple-insertion mechanism, which was attributed to the assistance of conductive rGO and ionic conductor LaPO_4 layer, with the ability to promote electronic transfer and Li^+ diffusion coefficient between active nanorods efficiently.

2. Experimental section

2.1 Synthesis of $\beta\text{-Li}_x\text{V}_2\text{O}_5$ nanorods

The $\beta\text{-Li}_x\text{V}_2\text{O}_5$ nanorods were obtained by a facile hydrothermal route followed by

calcination treatment.[15] Briefly, 0.1 g V_2O_5 and 3.0 g $LiNO_3$ were added into 30 mL de-ionized water with vigorously stirring. Then, the orange-yellow suspension was transferred into 50 mL Teflon-lined stainless autoclave and heated at 220 °C for 24 h. The precursor was collected by centrifugation and washed with absolute ethanol for several times, which was calcinated at 600 °C for 3 h under Ar atmosphere. The final product was denoted as LVO.

2.2 LaPO₄ coating and rGO wrapping

The surface modification of β - $Li_xV_2O_5$ nanorods was implemented by a two-step process involving chemical precipitation and frozen dryness. Firstly, 90 mg LVO powder was dispersed into 0.1 M $La(NO_3)_3 \cdot 6H_2O$ (Aldrich, 99.99%) and $NH_4H_2PO_4$ solution with continuous stirring for 24 h, which was evaporated at room temperature and calcinated at 400 °C for 3 h under Ar atmosphere. The corresponding products were denoted as $LaPO_4/LVO$. Subsequently, the obtained $LaPO_4/LVO$ powder was dispersed into 20 mL 0.5 M rGO solution by vigorous stirring, which was frozen quickly by liquid nitrogen and frozen dried overnight. The final product was obtained with heat treatment at 180 °C for 2 h under Ar atmosphere and labeled as rGO/ $LaPO_4/LVO$. Herein, the rGO nanosheets were prepared from natural graphite powders by Hummer's method.[27, 28]

2.3 Characterization of morphology and structure

The crystal structure of the obtained products was performed by X-ray diffraction (XRD, Rigaku D/Max2500 with $Cu K_\alpha$ radiation) and Raman spectra (Jobin Yvon Horiba with He-Ne laser, 632.9 nm). The morphology characterization was collected

by field-emission scanning electron microscope (FE-SEM, FEI Quanta 200F), and transmission electron microscope (TEM, JEM 2100, 200 kV), respectively. The chemical valence was analyzed by X-ray photoelectron spectroscopy (XPS, ThermoFisher). The binding energy of XPS was corrected by adjusting the C 1s photoelectron peak at 284.8 eV for the reference.

2.4 Electrochemical measurements

The electrochemical performance of β -Li_xV₂O₅ electrode before and after surface modification was evaluated using CR2025-type coin cells, which were assembled in an Ar-filled glovebox (Germany, MBraun) with the contents of H₂O and O₂ less than 5 ppm. The cathode was fabricated by mixing the active material, conductive agent and PVDF binder in the weight ratios of 8 : 1 : 1 and pasted onto Al foils, which was punched into round disk with diameter of 14 mm after vacuum dryness. 1 M LiPF₆ dissolved in ethylene carbonate/ethyl methyl carbonate/dimethylcarbonate (EC/EMC/DMC 1 : 1 : 1 in volume ratio) solvent was adopted as the electrolyte. The lithium metal was employed as the counter/reference electrode and the porous polypropylene films were served as separator, respectively.

The charge/discharge tests were carried out on LAND multi-channel battery testing system (CT2001A, Jinnuo Wuhan Corp., China) in the potential range of 1.8–4.0 V (vs. Li/Li⁺). Both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were operated on electrochemical workstation (CHI660E). The scan rate of CV was set as 0.05 mV s⁻¹ and the frequency of EIS ranged from 100 kHz to 0.01 Hz, respectively. For the SEM and XRD test of the cycled electrode, the

coin cells were disassembled in Ar-filled glove box and rinsed in DMC solvent repeatedly.

3. Results and discussion

3.1 Characterization of rGO/LaPO₄/LVO nanorods

In the crystal structure of β -Li_xV₂O₅ (Figure 1a), there are three different vanadium sites marked with different colours, namely, V(1), V(2), and V(3). The edge-sharing V(1)O₆ octahedra and corner-sharing V(2)O₆ octahedra constitute [V₄O₁₁]_n layers along the *b* axis in form of zigzag chains and double chains (projection along the *a*-axis in Figure 1b), respectively, and the five-fold V(3)O₅ pyramids chains were acted as pillars to connect the layers by corner-shared oxygen. The formed tunnel-like β phase vanadium oxide bronzes can facilely accommodate a large amount of Li⁺ by the successive filling of different crystallographic sites in the tunneled host structure. Whereas the complicated crystal structure is ease to be transformed by the partial reduction or oxidation of the framework vanadium atoms, giving rise to undesired impurity phase. The XRD pattern of the rGO/LVO sample prepared by oven-drying was provided in Figure S1. Obviously, strong diffraction of LiV₃O₈ phase was detected in the rGO/ β -Li_xV₂O₅ sample, suggesting the unstable phase structure when dried in heating environment with reduced graphene oxide nanosheets. By comparison, the XRD patterns of the rGO/LaPO₄/LVO sample obtained by gentle frozen dryness were displayed in Figure 1c. The hydrothermal synthesized product labeled as LVO were assigned to the

monoclinic $\beta\text{-Li}_x\text{V}_2\text{O}_5$ phase (JCPDS no. 73-1670). Noticeably, the modification samples of LaPO_4/LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$ exhibit identical diffraction peaks with that of $\beta\text{-Li}_x\text{V}_2\text{O}_5$ phase.[29] Herein, the well-preserved $\beta\text{-Li}_x\text{V}_2\text{O}_5$ phase after modification with electronic conductive rGO and ionic conductive LaPO_4 further demonstrate that the frozen dryness strategy was effective to be applied in the surface modification for the vanadate compound with complex valence states. Besides, the diffraction peak of rGO and LaPO_4 was absent in the XRD pattern, which was probably because of the relatively low diffraction intensity of rGO and trace amount of LaPO_4 .

The morphology of $\text{rGO}/\text{LaPO}_4/\text{LVO}$ was characterized by SEM and TEM, and the results are shown in Figure 1d-f. It can be clearly seen that the LVO nanorods were about 300–500 nm in average diameter and 1–1.5 μm in average length. LVO nanorods were well wrapped by reduced graphene oxide nanosheets without aggregation, which would bridge the electrical connection between the dispersed LVO nanorods effectively (Figure 1d). Noticeably, tiny nanoparticles were observed on the surface of LVO nanorods with LaPO_4 coating even if the rods are wrapped by rGO nanosheets. From TEM image in Figure 1e, it can be seen that the LVO nanorods were covered by a crystalline layer with thickness of about 20 nm. The high-resolution TEM image of LVO rods surface particle shown in Figure 1f presented a clear interplanar spacing lattice of 0.488 nm that was in agreement with the (110) crystal planes of the monoclinic LaPO_4 phase, further proving that LaPO_4 layer is successfully

coated onto the LVO surface. Meanwhile, the energy dispersive X-ray spectroscopy (EDX) mapping of rGO/LaPO₄/LVO was displayed in Figure S2. As shown, the elements La and P were detected, which exhibit almost the same distribution with the elements V and O. As shown, frozen dryness by liquid nitrogen freeze is a facile approach to realize the cooperation of reduced oxide graphene nanosheets with LVO rods.

Raman spectra of LVO and the rGO/LaPO₄/LVO sample were provided in Figure S3. Four prominent Raman bands around 143, 262, 514, 699 and 1005 cm⁻¹ were observed. The frequency mode of 143 and 262 cm⁻¹ in lower wavenumbers range was assigned to the bond bending vibrations and the frequency mode of 514, 699 and 1005 cm⁻¹ in higher wavenumbers range were designated to the stretching vibrations of differing V–O bonds, which was in good accordance with the Raman characteristic peaks of β -phase bronze Li_xV₂O₅ compounds.[15, 30] Besides, two typical D and G bands of graphene at 1340 and 1600 cm⁻¹ were presented in the rGO/LaPO₄/LVO composite, which originated from the defects of disordered sp² carbon atoms and graphite carbon, respectively.[31] The intensity ratio of I_D/I_G was estimated to be 0.99, suggesting the high quality of graphene in the rGO/LaPO₄/LVO composite.

The elemental valence states information in pristine LVO and modified samples were investigated by X-ray photoelectron spectroscopy. The XPS spectra of pristine LVO, LaPO₄/LVO and rGO/LaPO₄/LVO samples were provided in Figure 2a. As seen, the characteristic peak of lithium, vanadium and oxygen can be detected for all the prepared samples. Noticeably, the P2p peak centered at 102.1 eV and the La3d peak located around 836 eV can be observed on the XPS spectrum for LaPO₄/LVO and rGO/LaPO₄/LVO sample,

indicating the existence of LaPO_4 component after surface modification. The high-resolution $\text{V}2\text{p}$ spectra of the products before and after modification are displayed in Figure 2b. As shown, the $\text{V}2\text{p}$ spectrum was composed of two characteristic peaks of $\text{V}2\text{p}^{3/2}$ and $\text{V}2\text{p}^{1/2}$ located at 517.4 and 524.9 eV, respectively. Notably, both of the $\text{V}2\text{p}^{3/2}$ and $\text{V}2\text{p}^{1/2}$ peak can be deconvoluted into two components with the strong one from the pentavalent state (V^{5+}) and the weak one from the tetravalent state (V^{4+}). [32] Based on the peak areas, the ratio of V^{4+} to V^{5+} in LVO sample was calculated to be 0.218, which increase to 0.367 after surface modification with rGO and LaPO_4 . The slight increase of V^{4+} on the surface is reasonable because of the existence of reductive oxide graphene when annealed in the inert atmosphere, which might be beneficial for the electronic transfer with more pathways for electron hopping between V^{5+} and V^{4+} . [33] Additionally, the characteristic XPS peak of $\text{La}3\text{d}$ located at 839.0 eV along with a satellite peak around 835.8 eV was detected in the rGO/ LaPO_4 /LVO composites (Figure 2c), further verifying the existence of LaPO_4 coating layer. [34]

3.2 Electrochemical properties of rGO/ LaPO_4 /LVO cathode

In order to investigate the electrochemical behavior of $\beta\text{-Li}_x\text{V}_2\text{O}_5$ electrode after surface modification, the CV curves of LVO and rGO/ LaPO_4 /LVO electrodes were recorded at a scan rate of 0.05 mV s^{-1} in voltage range of 1.8–4.0 V (vs. Li/Li^+). As shown in Figure 3a, five distinct reduction peaks located at 3.60, 3.42, 2.87, 2.56, 1.90 V were observed for LVO electrode, corresponding to the Li^+ successive occupation processes of the specific lithium sites in tunneled framework. [14] For the pristine LVO electrode, large potential

gap of around 0.36 V was observed for the redox peaks located at 2.92/2.56 V. In comparison, smaller potential difference of 0.23 V was displayed for the rGO/LaPO₄/LVO composite, implying that the electrochemical polarization was significantly alleviated and the charge transfer reactivity was improved with the conductive rGO layer. The complicated multistep Li⁺ insertion/extraction processes in vanadate electrode were derived from the energy differences for Li-ion holding in different Li sites.[35] Noticeably, the redox peak pairs centered at 2.87/2.91 V was absent in the CV curves of pristine LVO electrode, indicating the difficult extractions of lithium ions from the β vanadium bronze structure, while that was clearly observed for rGO/LaPO₄/LVO electrode, further demonstrating that the multi-step intercalation and deintercalation of lithium ion in tunneled structure LVO was highly reversible with the presence of rGO and LaPO₄ layer. From the CV curves of rGO/LaPO₄/LVO electrode with sharper redox peak and smaller redox potential difference, we can conclude that the Li⁺ intercalation process was facilitated effectively by the assistance of rGO and LaPO₄ layer.

Next, the electrochemical performance of rGO/LaPO₄/LVO electrode were evaluated. The charge/discharge profiles of the LVO and rGO/LaPO₄/LVO electrodes cycled in the voltage window of 1.8–4.0 V at 60 mA g⁻¹ was plotted in Figure 3b and c. Five distinct discharge voltage plateaus around 3.6 V, 3.4 V, 2.8 V, 2.4 V and 1.9 V were observed, which was in good accordance with the CV curves, relating to the successive Li insertion steps into LVO tunneled

crystal structure. Noticeably, the primary charge/discharge potential gap for rGO/LaPO₄/LVO electrode (0.16 V) was much smaller than the LVO electrode (0.3 V), further implying the alleviated electrochemical reaction polarization by surface modification. Meanwhile, the multiple charge/discharge voltages for rGO/LaPO₄/LVO electrode were highly overlapped with clearly visible voltage plateaus during cycling (Figure 3c), which suffered from serious voltage decay for LVO electrode (Figure 3b), implying the gradual lithium trapping in the host lattice due to the sluggish Li⁺ diffusion kinetics. The elevated electrochemical kinetics was exclusively due to highly conductive graphene matrix with large area, which could effectively facilitate the electronic transfer by providing more electric contact area between the active LVO nanorods.[36, 37]

To provide an intuitive observation of the intricate Li ordering steps in β -Li_xV₂O₅, the crystal structure of β -Li_xV₂O₅ with possible Li⁺ tunnel sites was illustrated in Figure 3d. For the β -Li_xV₂O₅, the pre-inserted Li⁺ were randomly half-occupied in the tunnel sites that labeled M1 with the stoichiometric composition $x = 0.33$ according to Wadsley. [38] Meanwhile, there also existed three alternative interstitial sites for Li⁺ intercalation: eight-coordinated sites M2, tetrahedral sites M3, and octahedral sites M4 as shown in Figure 3d with different colors.[39] During the discharge process, the M2 and M3 sites would be half-occupied preferentially by inserted Li⁺ which was governed by the repulsive coulometric interactions between neighboring sites. When the M1, M2, M3 tunnel sites are fully occupied, the filling of octahedral sites M4 would

be possible, which corresponds to the last voltage plateau as shown in Figure 3b. Of particular note, the Li^+ filling step of M4 sites with the voltage plateau around 2 V was well-maintained for the rGO/LaPO₄/LVO electrode even after 100 cycles, further demonstrating the enhanced electrochemical reaction dynamics in $\beta\text{-Li}_x\text{V}_2\text{O}_5$ after surface modification.

Further, the cycling performance of LVO and rGO/LaPO₄/LVO electrodes at a current density of 60 mA g⁻¹ was evaluated as shown in Figure 3e. The pristine LVO electrode delivered an initial discharge capacity of 282.5 mAh g⁻¹, whereas suffered from serious capacity decay with relatively low capacity retention of 37.3% after 100 cycles. The severe capacity fades mainly originated from the poor intrinsic conductivity as well as potential vanadium dissolution for pristine LVO particles.[40] It was worth mentioning that the cyclic stability of LVO was enhanced dramatically when the coating of LaPO₄ and rGO layer was introduced, which delivered high capacity retention up to 84.1% at a slight expense of specific capacity (275.7 mAh g⁻¹). The cyclic stability of LVO electrode was boosted with the surface modified by protective and conductive layer, which was probably derived from the protective coating layer with the ability to prevent the electrode from electrolyte erosion as well as stabilize the crystal structure.[41]

On the other hand, surface modification with conductive rGO and ionic conductive LaPO₄ is expected to facilitate the electrochemical reaction dynamics, so we also explore the rate capability of LVO and rGO/LaPO₄/LVO electrodes at different charge/discharge current densities as shown in Figure 3f. The LVO sample delivers specific discharge capacities of 321.9, 252.4, 193.7, 139.2, 93.4 and 48.2 mAh g⁻¹ at current densities of 15, 30, 60, 100, 200 and 400 mA g⁻¹, respectively. Significant capacity decay was exhibited for pristine LVO electrode with the current density

increasing. For the case of rGO/LaPO₄/LVO electrode, the specific discharge capacities were 315.8, 263.2, 226.3, 203.3, 186.6 and 170.3 mAh g⁻¹ at current densities of 15, 30, 60, 100, 200 and 400 mA g⁻¹, respectively. When the current density was set back to 15 mA g⁻¹, as high as 291.3 mAh g⁻¹ can be recovered for the rGO/LaPO₄/LVO electrode. It was worth to mention that the capacity varied slightly under every current density for the modification sample. In order to make an intuitive observation of the improved rate capability for modification electrode, the discharge curves of the LVO and rGO/LaPO₄/LVO electrode at different current densities were displayed in Figure S4a and b. Five discharge plateaus corresponding to the successive Li ordering processes in the β tunnel framework were observed evidently on the discharge profiles for LVO electrode at 15 mA g⁻¹, which experienced noticeable voltage recession with the growing current density, implying the gradual capacity loss derived from lithium trapping in the host lattice due to the sluggish Li⁺ diffusion kinetics especially under high current densities.[42] For comparison, the discharge plateau was still distinct for rGO/LaPO₄/LVO electrode at current density up to 400 mA g⁻¹, which is capable of delivering ~75% of the reversible capacity discharged at 60 mA g⁻¹, further suggesting the dramatically improved rate capability of LVO electrode with surface modification. The high rate capability and stable cyclability makes the rGO/LaPO₄/LVO composite competitive candidate for lithium ion batteries applications.

3.3 Mechanism insight of electrochemical performance improvement

To further clarify the improved electrochemical performance of rGO/LaPO₄/LVO electrode, EIS was carried out to analyze the variation of electrode/electrolyte interface property during cycling. The Nyquist plots of LVO and rGO/LaPO₄/LVO electrode after initial cycling were provided in Figure 4a. Both of the curves were composed of a semicircle in the high frequency followed by a straight line in the low

frequency region, which are assigned to the charge transfer resistance (R_{ct}) on the electrode/electrolyte interface and the Li^+ diffusion within the bulk electrode materials, respectively.[43, 44] The resistance values of the LVO and rGO/LaPO₄/LVO electrodes were fitted by the equivalent circuit inset in Figure 4a. The fitting data were shown in **Table 1**. Obviously, the R_{ct} value of rGO/LaPO₄/LVO (98.2 Ω) is three times lower than that of the LVO electrode (379.8 Ω), implying the charge transfer resistance was reduced effectively upon rGO modification. Even after 100 cycles (shown in Figure 4b), the rGO/LaPO₄/LVO electrode still exhibits much lower R_{ct} than that of the LVO electrode, further indicating that the introduction of rGO and LaPO₄ layer could stabilize the electrode/electrolyte interface, which contribute to the superior cyclic stability and rate capability during charge/discharge processes. The Li ion diffusion coefficient can be calculated by the following equation:[45]

$$D_{\text{Li}^+} = 0.5R^2T^2 / S^2n^4F^4C^2\sigma^2$$

where R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature (298 K), S is the electrode area (1.54 cm²), n is the number of electron transfer, F is the Faraday constant (96500 C mol⁻¹), C is the molar concentration of the Li^+ in the cathode calculated on the basis of the crystallographic cell parameter of LVO, and σ is the Warburg impedance coefficient obtained from the slope of fitting lines as shown in Figure 4c. The Li^+ diffusion coefficient of rGO/LaPO₄/LVO is calculated to be 4.67×10^{-14} cm² s⁻¹, which is approximately one order higher than that of pristine LVO (2.08×10^{-15} cm² s⁻¹). The evidently increased Li^+ diffusion coefficient suggests that the surface layer of LaPO₄ is favorable to accelerate the diffusion of lithium ions and enhance the reversibility of lithium ion insertion/extraction in tunnel structure.[46]

To highlight the advantages of surface engineering on LVO electrode, the differential capacity (dQ/dV) plots of LVO and rGO/LaPO₄/LVO electrodes after 100

cycles were presented in Figure 4d. Obviously, strong and sharp redox peaks were still observed evidently on the dQ/dV curves for the rGO/LaPO₄/LVO electrode even after 100 cycles, which almost disappeared for the pristine LVO accompanied by serious capacity decay, further revealing that surface co-modification was effective to improve the reversibility of repeated lithium ion insertion/extraction in LVO cathode.

Furthermore, XRD and SEM characterization was utilized to investigate the change of crystal structure and morphology during cycling. Figure 5a shows the XRD patterns of the LVO and rGO/LaPO₄/LVO electrodes before and after 100 cycles. For the cycled LVO electrode, the main diffraction peak intensity of (002) plane was rather weak, which was still maintained sharp and strong for the modified LVO electrode, suggesting the crystal structure was well-preserved upon cycling, which was primarily benefited by the effective protection of crystal structure from electrolyte corrosion by surface modification layer. Figure 5c and e shows the SEM images of the LVO and rGO/LaPO₄/LVO electrodes after 100 cycles. Inevitably, cracks occurred on the LVO nanorods surface induced by the structural stress during lithiation processes, while intact nanorod surface was preserved for rGO/LaPO₄/LVO electrodes even after long-term cycling as shown in Figure 5e, further verifying the improved structural stability and reversibility for the modified LVO electrode.

Based on above discussion, the interfacial schematic illustration of LVO with rGO and LaPO₄ surface layer is schematically demonstrated in Figure 6. The LVO nanorods was distributed uniformly on the conductive rGO matrix. During discharge process, the electronic transmission between the active LVO nanorods was promoted efficiently through rGO layer which act as “bridge” to connect the adjacent LVO nanorods together. Meanwhile, the interfacial Li⁺ diffusion between the bulk LVO electrode and electrolyte was also facilitated by the LaPO₄ layer, which was favorable for the excellent rate capability. Additionally, the protective layer of LaPO₄ and rGO

would stabilize the electrode/electrolyte interface and protect the LVO particles from electrolyte corrosion, contributing to the improved structural stability and cyclic stability during repeated Li insertion/extraction processes.

4. Conclusions

To summarize, we successfully prepared rGO/LaPO₄/Li_xV₂O₅ composite electrode via chemical precipitation and frozen dryness. The rGO/LaPO₄/LVO composite demonstrated significantly improved cyclic stability and rate capability. At a current density of 60 mA g⁻¹, the rGO/LaPO₄/LVO electrode delivered high reversible capacity of 275.7 mAh g⁻¹ with high capacity retention of 84.1% after 100 cycles. The enhanced electrochemical performance of the LVO electrode is ascribed to the promoted electronic transfer and Li⁺ diffusion coefficient between active nanorods with the functionality of conductive rGO and LaPO₄ layer. The excellent electrochemical properties of rGO/LaPO₄/LVO composites, together with their high specific capacity and rate capability, make tunneled lithium vanadate promising candidate for next-generation rechargeable lithium ion batteries.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version.

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Figures and Captions:

Figure 1 Crystal structure and morphology characterization. (a, b) Crystal structure of β - $\text{Li}_x\text{V}_2\text{O}_5$ with different projections along b and a -axis, respectively. V1 represent the edge-sharing VO_6 octahedra, V2 represents the corner-sharing VO_6 octahedra, and V3 represents the VO_5 pyramids. (c) XRD patterns of LVO, LaPO_4/LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$. The standard patterns of $\text{Li}_{0.33}\text{V}_2\text{O}_5$ is shown in the lower panel. (d) SEM, (e) TEM and (f) HRTEM images of LaPO_4 -coated LVO nanorods wrapped by rGO nanosheets. Inset in (e) is enlarged view of the interface.

Figure 2 XPS spectra of LVO, LaPO_4/LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$. (a) Survey spectra; (b) V2p; (c) core-level XPS spectra of La3d.

Figure 3 Electrochemical performance of LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrodes. (a) CV curves at scan rate of 0.05 mV s^{-1} . (b) Charge/discharge curves of LVO electrode. (c) Charge/discharge curves of $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrode. (d) Crystal structure of β - $\text{Li}_x\text{V}_2\text{O}_5$ with four possible tunnel sites for the inserted Li^+ in the β structure marked with different colors. (e) Cycling performance at current density of 60 mA g^{-1} . (f) Rate capability at current densities of 15 to 400 mA g^{-1} .

Figure 4 Electrochemical impedance spectrum analysis before and after 100 cycles. (a) Nyquist plots of LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrodes after initial cycles. Inset is the equivalent circuit for EIS fitting. (b) Nyquist plots of LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrodes after 100 cycles. (c) The relationship between Z' and $\omega^{-1/2}$ in the low-frequency range. (d) Differential capacity (dQ/dV) curves of LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrodes after 100 cycles.

Figure 5 Structural and morphology characterization of LVO electrode upon cycling. (a) XRD pattern with magnified patterns of the LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrodes after 100 cycles. (b) and (c) SEM images of the LVO electrodes before and after 100

cycles. (d) and (e) SEM images of the rGO/LaPO₄/LVO electrode before and after 100 cycles.

Figure 6 The interfacial schematic diagram of LVO electrode with rGO and LaPO₄ layer, which provide effective electronic transport path and protect electrode surface from electrolyte corrosion.

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Table 1. EIS fitting data of LVO and rGO/LaPO₄/LVO after 1st and 100th cycles

Cycles	LVO	LVO	rGO/LaPO ₄ /LVO	rGO/LaPO ₄ /LVO
	R_{sei}/Ω	R_{ct}/Ω	R_{sei}/Ω	R_{ct}/Ω
1st	45.5	379.8	37.4	98.2
100th	963.2	970.2	555.8	634.5

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Boosting the rate and cycling performance of β -Li_xV₂O₅ nanorods for Li ion battery by electrode surface decoration

Pan-Pan Wang^{a,b,c}, Yue Du^{a,c}, Bao-You Zhang^b, Yan-Xin Yao^b, Yu-Chen Xiao^b, Li-Jie Ci^a, Cheng-Yan Xu^{a,b,c,*}, Liang Zhen^{a,b,c,*}

^a School of Materials Science and Engineering, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China

^b School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

^c MOE Key Laboratory of Micro-Systems and Micro-Structures Manufacturing, Harbin Institute of Technology, Harbin 150080, China

E-mail: lzhen@hit.edu.cn (L.Z.); cy_xu@hit.edu.cn (C.Y.X.)

Abstract: The β -phase lithium vanadium oxide bronze (β -Li_xV₂O₅) with high theoretic specific capacity up to 440 mAh g⁻¹ is considered as promising cathode materials, however, their practical application is hindered by its poor ionic and electronic conductivity, resulting in unsatisfied cyclic stability and rate capability. Herein, we report the surface decoration of β -Li_xV₂O₅ cathode using both reduced oxide graphene and ionic conductor LaPO₄, which significantly promotes the electronic transfer and Li⁺ diffusion rate, respectively. As a result, the rGO/LaPO₄/Li_xV₂O₅ composite exhibits excellent electrochemical performance in terms of high reversible specific capacity of 275.7 mAh g⁻¹ with high capacity retention of 84.1% after 100 cycles at a current density of 60 mA g⁻¹, and acceptable

specific capacity of 170.3 mAh g⁻¹ at high current density of 400 mA g⁻¹. The cycled electrode is also analyzed by electrochemical impedance spectroscopy, *ex-situ* X-ray diffraction and scanning electron microscope, providing further insights into the improvement of electrochemical performance. Our results provide an effective approach to boost the electrochemical properties of lithium vanadates for practical application in lithium ion batteries.

Keywords: β -Li_xV₂O₅, cyclic stability, reduced oxide graphene, ionic conductor, surface decoration

1. Introduction

Due to the attractive merits of high energy density, long cyclic life and environmental friendliness, rechargeable lithium ion batteries (LIBs) have been widely used as power source for portable electronic devices.[1-3] Despite that, the energy and power density of current commercial LIBs was still far from satisfying the urgent requirements for further applications in electric vehicles and smart grids. The limited capacity of commonly used cathodes, including LiCoO₂, LiFePO₄, LiMn₂O₄ and Li-excess layered oxide compounds, is the main limiting factor for the realization of high energy-density LIBs, which delivered lower reversible capacities (<280 mAh g⁻¹) than the counterpart graphite anode. To this end, cathode material with higher specific capacity are urgently needed to meet the ever-increasing goals for high energy-density LIBs.[4, 5]

Recently, vanadium oxides and their derivatives have received tremendous attention due to their rich chemistry and high specific capacity as LIBs

cathode.[6-8] As for V_2O_5 , its theoretical capacity reaches up to 440 mAh g^{-1} because more than 3 lithium ions per formula can be inserted into V_2O_5 layer, whereas the capacity of V_2O_5 cathode decays seriously after initial cycling due to the irreversible phase transformation and local structure collapse when the lithium uptakes more than 2 moles per formula unit.[9, 10] Different from layered V_2O_5 , β -phase vanadium oxide bronzes ($\beta\text{-M}_xV_2O_5$, M = alkali, alkaline earth, and transition metals) adopts more stable and rigid crystal structures with the $[VO_6]$ octahedrons layers pillared by $[VO_5]$ square pyramids.[11] The unique 3D framework contained several feasible interstitial sites in the tunnel structure, endowing the vanadium oxide bronzes rather good structural reversibility upon large amount of lithium accommodation, while maintaining high capacity features. [12-15] Despite these advantages, one major drawback of pure β -phase vanadate cathode is its inferior rate capability and cycling stability,[16, 17] which was believed to be related with its intrinsic poor electronic conductivity and relatively slow Li^+ diffusion kinetic, especially upon deep lithiation. Meanwhile, the fragile interfacial property of pristine vanadate electrode with the risk of erosion from the electrolytes and vanadium dissolution is considered to be another reason for capacity fading.[18] Thus, modification strategies are imperative to overcome these limitations, thereby boosting the electrochemical properties of lithium vanadate cathode.[19]

Surface modification with conducting materials (e.g., graphene,[20, 21] polymer,[22, 23]) or ionic conductors (phosphates,[24] metal oxides,[25, 26]

etc.) is proved to be efficient to enhance the electrochemical properties of vanadate oxide cathode. Recently, two-dimensional graphene-based materials were emerging as an eye-catching coating candidate with superior electrical conductivity, which was usually hybrid with active materials through hydrothermal route or calcination treatment in reductive atmosphere. Whereas the coexisted V^{4+} and V^{5+} in $\beta\text{-Li}_x\text{V}_2\text{O}_5$ are susceptible to the reductive graphene during the hybridization process especially under high calcination temperature, resulting in undesired impurity phase or even inducing irreversible phase transition and thus capacity loss of the cathode. To achieve a uniform graphene coating layer on $\beta\text{-Li}_x\text{V}_2\text{O}_5$ with complex valence states while maintain the $\beta\text{-Li}_x\text{V}_2\text{O}_5$ phase is still a big challenge. Herein, a gentle freeze drying strategy with ionic conductor decoration was applied successfully to tackle these issues.

In this work, the conductive reduced oxide graphene (rGO) and ionic conductor LaPO_4 were employed to engineer the interfacial chemistry of $\beta\text{-Li}_x\text{V}_2\text{O}_5$ cathode via chemical precipitation route followed by frozen dryness. The obtained rGO/ LaPO_4 /LVO electrode demonstrated remarkable cycling stability and superior rate capability with specific Li^+ multiple-insertion mechanism, which was attributed to the assistance of conductive rGO and ionic conductor LaPO_4 layer, with the ability to promote electronic transfer and Li^+ diffusion coefficient between active nanorods efficiently.

2. Experimental section

2.1 Synthesis of β -Li_xV₂O₅ nanorods

The β -Li_xV₂O₅ nanorods were obtained by a facile hydrothermal route followed by calcination treatment.[15] Briefly, 0.1 g V₂O₅ and 3.0 g LiNO₃ were added into 30 mL de-ionized water with vigorously stirring. Then, the orange-yellow suspension was transferred into 50 mL Teflon-lined stainless autoclave and heated at 220 °C for 24 h. The precursor was collected by centrifugation and washed with absolute ethanol for several times, which was calcinated at 600 °C for 3 h under Ar atmosphere. The final product was denoted as LVO.

2.2 LaPO₄ coating and rGO wrapping

The surface modification of β -Li_xV₂O₅ nanorods was implemented by a two-step process involving chemical precipitation and frozen dryness. Firstly, 90 mg LVO powder was dispersed into 0.1 M La(NO₃)₃·6H₂O (Aldrich, 99.99%) and NH₄H₂PO₄ solution with continuous stirring for 24 h, which was evaporated at room temperature and calcinated at 400 °C for 3 h under Ar atmosphere. The corresponding products were denoted as LaPO₄/LVO. Subsequently, the obtained LaPO₄/LVO powder was dispersed into 20 mL 0.5 M rGO solution by vigorous stirring, which was frozen quickly by liquid nitrogen and frozen dried overnight. The final product was obtained with heat treatment at 180 °C for 2 h under Ar atmosphere and labeled as rGO/LaPO₄/LVO. Herein, the rGO nanosheets were prepared from natural graphite powders by Hummer's method.[27, 28]

2.3 Characterization of morphology and structure

The crystal structure of the obtained products was performed by X-ray diffraction

(XRD, Rigaku D/Max2500 with Cu K_{α} radiation) and Raman spectra (Jobin Yvon Horiba with He-Ne laser, 632.9 nm). The morphology characterization was collected by field-emission scanning electron microscope (FE-SEM, FEI Quanta 200F), and transmission electron microscope (TEM, JEM 2100, 200 kV), respectively. The chemical valence was analyzed by X-ray photoelectron spectroscopy (XPS, ThermoFisher). The binding energy of XPS was corrected by adjusting the C 1s photoelectron peak at 284.8 eV for the reference.

2.4 Electrochemical measurements

The electrochemical performance of β - $\text{Li}_x\text{V}_2\text{O}_5$ electrode before and after surface modification was evaluated using CR2025-type coin cells, which were assembled in an Ar-filled glovebox (Germany, MBraun) with the contents of H_2O and O_2 less than 5 ppm. The cathode was fabricated by mixing the active material, conductive agent and PVDF binder in the weight ratios of 8 : 1 : 1 and pasted onto Al foils, which was punched into round disk with diameter of 14 mm after vacuum dryness. 1 M LiPF_6 dissolved in ethylene carbonate/ethyl methyl carbonate/dimethylcarbonate (EC/EMC/DMC 1 : 1 : 1 in volume ratio) solvent was adopted as the electrolyte. The lithium metal was employed as the counter/reference electrode and the porous polypropylene films were served as separator, respectively.

The charge/discharge tests were carried out on LAND multi-channel battery testing system (CT2001A, Jinnuo Wuhan Corp., China) in the potential range of 1.8–4.0 V (vs. Li/Li^+). Both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were operated on electrochemical workstation (CHI660E).

The scan rate of CV was set as 0.05 mV s^{-1} and the frequency of EIS ranged from 100 kHz to 0.01 Hz, respectively. For the SEM and XRD test of the cycled electrode, the coin cells were disassembled in Ar-filled glove box and rinsed in DMC solvent repeatedly.

3. Results and discussion

3.1 Characterization of rGO/LaPO₄/LVO nanorods

In the crystal structure of $\beta\text{-Li}_x\text{V}_2\text{O}_5$ (Figure 1a), there are three different vanadium sites marked with different colours, namely, V(1), V(2), and V(3). The edge-sharing V(1)O₆ octahedra and corner-sharing V(2)O₆ octahedra constitute [V₄O₁₁]_n layers along the *b* axis in form of zigzag chains and double chains (projection along the *a*-axis in Figure 1b), respectively, and the five-fold V(3)O₅ pyramids chains were acted as pillars to connect the layers by corner-shared oxygen. The formed tunnel-like β phase vanadium oxide bronzes can facilely accommodate a large amount of Li⁺ by the successive filling of different crystallographic sites in the tunneled host structure. Whereas the complicated crystal structure is ease to be transformed by the partial reduction or oxidation of the framework vanadium atoms, giving rise to undesired impurity phase. The XRD pattern of the rGO/LVO sample prepared by oven-drying was provided in Figure S1. Obviously, strong diffraction of LiV₃O₈ phase was detected in the rGO/ $\beta\text{-Li}_x\text{V}_2\text{O}_5$ sample, suggesting the unstable phase structure when dried in heating environment with reduced graphene oxide nanosheets. By comparison, the XRD patterns of the

rGO/LaPO₄/LVO sample obtained by gentle frozen dryness were displayed in Figure 1c. The hydrothermal synthesized product labeled as LVO were assigned to the monoclinic β -Li_xV₂O₅ phase (JCPDS no. 73-1670). Noticeably, the modification samples of LaPO₄/LVO and rGO/LaPO₄/LVO exhibit identical diffraction peaks with that of β -Li_xV₂O₅ phase.[29] Herein, the well-preserved β -Li_xV₂O₅ phase after modification with electronic conductive rGO and ionic conductive LaPO₄ further demonstrate that the frozen dryness strategy was effective to be applied in the surface modification for the vanadate compound with complex valence states. Besides, the diffraction peak of rGO and LaPO₄ was absent in the XRD pattern, which was probably because of the relatively low diffraction intensity of rGO and trace amount of LaPO₄.

The morphology of rGO/LaPO₄/LVO was characterized by SEM and TEM, and the results are shown in Figure 1d-f. It can be clearly seen that the LVO nanorods were about 300–500 nm in average diameter and 1–1.5 μ m in average length. LVO nanorods were well wrapped by reduced graphene oxide nanosheets without aggregation, which would bridge the electrical connection between the dispersed LVO nanorods effectively (Figure 1d). Noticeably, tiny nanoparticles were observed on the surface of LVO nanorods with LaPO₄ coating even if the rods are wrapped by rGO nanosheets. From TEM image in Figure 1e, it can be seen that the LVO nanorods were covered by a crystalline layer with thickness of about 20 nm. The high-resolution TEM image of LVO rods surface particle shown in Figure 1f presented a clear interplanar spacing

lattice of 0.488 nm that was in agreement with the (110) crystal planes of the monoclinic LaPO_4 phase, further proving that LaPO_4 layer is successfully coated onto the LVO surface. Meanwhile, the energy dispersive X-ray spectroscopy (EDX) mapping of rGO/ LaPO_4 /LVO was displayed in Figure S2. As shown, the elements La and P were detected, which exhibit almost the same distribution with the elements V and O. As shown, frozen dryness by liquid nitrogen freeze is a facile approach to realize the cooperation of reduced oxide graphene nanosheets with LVO rods.

Raman spectra of LVO and the rGO/ LaPO_4 /LVO sample were provided in Figure S3. Four prominent Raman bands around 143, 262, 514, 699 and 1005 cm^{-1} were observed. The frequency mode of 143 and 262 cm^{-1} in lower wavenumbers range was assigned to the bond bending vibrations and the frequency mode of 514, 699 and 1005 cm^{-1} in higher wavenumbers range were designated to the stretching vibrations of differing V–O bonds, which was in good accordance with the Raman characteristic peaks of β -phase bronze $\text{Li}_x\text{V}_2\text{O}_5$ compounds.[15, 30] Besides, two typical D and G bands of graphene at 1340 and 1600 cm^{-1} were presented in the rGO/ LaPO_4 /LVO composite, which originated from the defects of disordered sp^2 carbon atoms and graphite carbon, respectively.[31] The intensity ratio of I_D/I_G was estimated to be 0.99, suggesting the high quality of graphene in the rGO/ LaPO_4 /LVO composite.

The elemental valence states information in pristine LVO and modified samples were investigated by X-ray photoelectron spectroscopy. The XPS spectra of pristine LVO, LaPO_4 /LVO and rGO/ LaPO_4 /LVO samples were provided in Figure 2a. As seen, the characteristic peak of lithium, vanadium and

oxygen can be detected for all the prepared samples. Noticeably, the P2p peak centered at 102.1 eV and the La3d peak located around 836 eV can be observed on the XPS spectrum for LaPO₄/LVO and rGO/LaPO₄/LVO sample, indicating the existence of LaPO₄ component after surface modification. The high-resolution V2p spectra of the products before and after modification are displayed in Figure 2b. As shown, the V2p spectrum was composed of two characteristic peaks of V2p^{3/2} and V2p^{1/2} located at 517.4 and 524.9 eV, respectively. Notably, both of the V2p^{3/2} and V2p^{1/2} peak can be deconvoluted into two components with the strong one from the pentavalent state (V⁵⁺) and the weak one from the tetravalent state (V⁴⁺).[32] Based on the peak areas, the ratio of V⁴⁺ to V⁵⁺ in LVO sample was calculated to be 0.218, which increase to 0.367 after surface modification with rGO and LaPO₄. The slight increase of V⁴⁺ on the surface is reasonable because of the existence of reductive oxide graphene when annealed in the inert atmosphere, which might be beneficial for the electronic transfer with more pathways for electron hopping between V⁵⁺ and V⁴⁺. [33] Additionally, the characteristic XPS peak of La3d located at 839.0 eV along with a satellite peak around 835.8 eV was detected in the rGO/LaPO₄/LVO composites (Figure 2c), further verifying the existence of LaPO₄ coating layer.[34]

3.2 Electrochemical properties of rGO/LaPO₄/LVO cathode

In order to investigate the electrochemical behavior of β -Li_xV₂O₅ electrode after surface modification, the CV curves of LVO and rGO/LaPO₄/LVO electrodes were recorded at a scan rate of 0.05 mV s⁻¹ in voltage range of 1.8–4.0 V (vs. Li/Li⁺). As shown in Figure 3a, five distinct reduction peaks

located at 3.60, 3.42, 2.87, 2.56, 1.90 V were observed for LVO electrode, corresponding to the Li^+ successive occupation processes of the specific lithium sites in tunneled framework.[14] For the pristine LVO electrode, large potential gap of around 0.36 V was observed for the redox peaks located at 2.92/2.56 V. In comparison, smaller potential difference of 0.23 V was displayed for the rGO/LaPO₄/LVO composite, implying that the electrochemical polarization was significantly alleviated and the charge transfer reactivity was improved with the conductive rGO layer. The complicated multistep Li^+ insertion/extraction processes in vanadate electrode were derived from the energy differences for Li-ion holding in different Li sites.[35] Noticeably, the redox peak pairs centered at 2.87/2.91 V was absent in the CV curves of pristine LVO electrode, indicating the difficult extractions of lithium ions from the β vanadium bronze structure, while that was clearly observed for rGO/LaPO₄/LVO electrode, further demonstrating that the multi-step intercalation and deintercalation of lithium ion in tunneled structure LVO was highly reversible with the presence of rGO and LaPO₄ layer. From the CV curves of rGO/LaPO₄/LVO electrode with sharper redox peak and smaller redox potential difference, we can conclude that the Li^+ intercalation process was facilitated effectively by the assistance of rGO and LaPO₄ layer.

Next, the electrochemical performance of rGO/LaPO₄/LVO electrode were evaluated. The charge/discharge profiles of the LVO and rGO/LaPO₄/LVO electrodes cycled in the voltage window of 1.8–4.0 V at 60 mA g⁻¹ was plotted

in Figure 3b and c. Five distinct discharge voltage plateaus around 3.6 V, 3.4 V, 2.8 V, 2.4 V and 1.9 V were observed, which was in good accordance with the CV curves, relating to the successive Li insertion steps into LVO tunneled crystal structure. Noticeably, the primary charge/discharge potential gap for rGO/LaPO₄/LVO electrode (0.16 V) was much smaller than the LVO electrode (0.3 V), further implying the alleviated electrochemical reaction polarization by surface modification. Meanwhile, the multiple charge/discharge voltages for rGO/LaPO₄/LVO electrode were highly overlapped with clearly visible voltage plateaus during cycling (Figure 3c), which suffered from serious voltage decay for LVO electrode (Figure 3b), implying the gradual lithium trapping in the host lattice due to the sluggish Li⁺ diffusion kinetics. The elevated electrochemical kinetics was exclusively due to highly conductive graphene matrix with large area, which could effectively facilitate the electronic transfer by providing more electric contact area between the active LVO nanorods.[36, 37]

To provide an intuitive observation of the intricate Li ordering steps in β -Li_xV₂O₅, the crystal structure of β -Li_xV₂O₅ with possible Li⁺ tunnel sites was illustrated in Figure 3d. For the β -Li_xV₂O₅, the pre-inserted Li⁺ were randomly half-occupied in the tunnel sites that labeled M1 with the stoichiometric composition $x = 0.33$ according to Wadsley. [38] Meanwhile, there also existed three alternative interstitial sites for Li⁺ intercalation: eight-coordinated sites M2, tetrahedral sites M3, and octahedral sites M4 as shown in Figure 3d with

different colors.[39] During the discharge process, the M2 and M3 sites would be half-occupied preferentially by inserted Li^+ which was governed by the repulsive coulometric interactions between neighboring sites. When the M1, M2, M3 tunnel sites are fully occupied, the filling of octahedral sites M4 would be possible, which corresponds to the last voltage plateau as shown in Figure 3b. Of particular note, the Li^+ filling step of M4 sites with the voltage plateau around 2 V was well-maintained for the rGO/LaPO₄/LVO electrode even after 100 cycles, further demonstrating the enhanced electrochemical reaction dynamics in $\beta\text{-Li}_x\text{V}_2\text{O}_5$ after surface modification.

Further, the cycling performance of LVO and rGO/LaPO₄/LVO electrodes at a current density of 60 mA g⁻¹ was evaluated as shown in Figure 3e. The pristine LVO electrode delivered an initial discharge capacity of 282.5 mAh g⁻¹, whereas suffered from serious capacity decay with relatively low capacity retention of 37.3% after 100 cycles. The severe capacity fades mainly originated from the poor intrinsic conductivity as well as potential vanadium dissolution for pristine LVO particles.[40] It was worth mentioning that the cyclic stability of LVO was enhanced dramatically when the coating of LaPO₄ and rGO layer was introduced, which delivered high capacity retention up to 84.1% at a slight expense of specific capacity (275.7 mAh g⁻¹). The cyclic stability of LVO electrode was boosted with the surface modified by protective and conductive layer, which was probably derived from the protective coating layer with the ability to prevent the electrode from electrolyte erosion as well as stabilize the crystal structure.[41]

On the other hand, surface modification with conductive rGO and ionic conductive LaPO₄ is expected to facilitate the electrochemical reaction dynamics, so we also

explore the rate capability of LVO and rGO/LaPO₄/LVO electrodes at different charge/discharge current densities as shown in Figure 3f. The LVO sample delivers specific discharge capacities of 321.9, 252.4, 193.7, 139.2, 93.4 and 48.2 mAh g⁻¹ at current densities of 15, 30, 60, 100, 200 and 400 mA g⁻¹, respectively. Significant capacity decay was exhibited for pristine LVO electrode with the current density increasing. For the case of rGO/LaPO₄/LVO electrode, the specific discharge capacities were 315.8, 263.2, 226.3, 203.3, 186.6 and 170.3 mAh g⁻¹ at current densities of 15, 30, 60, 100, 200 and 400 mA g⁻¹, respectively. When the current density was set back to 15 mA g⁻¹, as high as 291.3 mAh g⁻¹ can be recovered for the rGO/LaPO₄/LVO electrode. It was worth to mention that the capacity varied slightly under every current density for the modification sample. In order to make an intuitive observation of the improved rate capability for modification electrode, the discharge curves of the LVO and rGO/LaPO₄/LVO electrode at different current densities were displayed in Figure S4a and b. Five discharge plateaus corresponding to the successive Li ordering processes in the β tunnel framework were observed evidently on the discharge profiles for LVO electrode at 15 mA g⁻¹, which experienced noticeable voltage recession with the growing current density, implying the gradual capacity loss derived from lithium trapping in the host lattice due to the sluggish Li⁺ diffusion kinetics especially under high current densities.[42] For comparison, the discharge plateau was still distinct for rGO/LaPO₄/LVO electrode at current density up to 400 mA g⁻¹, which is capable of delivering ~75% of the reversible capacity discharged at 60 mA g⁻¹, further suggesting the dramatically improved rate capability of LVO electrode with surface modification. The high rate capability and stable cyclability makes the rGO/LaPO₄/LVO composite competitive candidate for lithium ion batteries applications.

3.3 Mechanism insight of electrochemical performance improvement

To further clarify the improved electrochemical performance of rGO/LaPO₄/LVO electrode, EIS was carried out to analyze the variation of electrode/electrolyte interface property during cycling. The Nyquist plots of LVO and rGO/LaPO₄/LVO electrode after initial cycling were provided in Figure 4a. Both of the curves were composed of a semicircle in the high frequency followed by a straight line in the low frequency region, which are assigned to the charge transfer resistance (R_{ct}) on the electrode/electrolyte interface and the Li⁺ diffusion within the bulk electrode materials, respectively.[43, 44] The resistance values of the LVO and rGO/LaPO₄/LVO electrodes were fitted by the equivalent circuit inset in Figure 4a. The fitting data were shown in **Table 1**. Obviously, the R_{ct} value of rGO/LaPO₄/LVO (98.2 Ω) is three times lower than that of the LVO electrode (379.8 Ω), implying the charge transfer resistance was reduced effectively upon rGO modification. Even after 100 cycles (shown in Figure 4b), the rGO/LaPO₄/LVO electrode still exhibits much lower R_{ct} than that of the LVO electrode, further indicating that the introduction of rGO and LaPO₄ layer could stabilize the electrode/electrolyte interface, which contribute to the superior cyclic stability and rate capability during charge/discharge processes. The Li ion diffusion coefficient can be calculated by the following equation:[45]

$$D_{Li^+} = 0.5R^2T^2 / S^2n^4F^4C^2\sigma^2$$

where R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature (298 K), S is the electrode area (1.54 cm²), n is the number of electron transfer, F is the Faraday constant (96500 C mol⁻¹), C is the molar concentration of the Li⁺ in the cathode calculated on the basis of the crystallographic cell parameter of LVO, and σ is the Warburg impedance coefficient obtained from the slope of fitting lines as shown in Figure 4c. The Li⁺ diffusion coefficient of rGO/LaPO₄/LVO is calculated to be

$4.67 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$, which is approximately one order higher than that of pristine LVO ($2.08 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$). The evidently increased Li^+ diffusion coefficient suggests that the surface layer of LaPO_4 is favorable to accelerate the diffusion of lithium ions and enhance the reversibility of lithium ion insertion/extraction in tunnel structure.[46]

To highlight the advantages of surface engineering on LVO electrode, the differential capacity (dQ/dV) plots of LVO and $\text{rGO/LaPO}_4/\text{LVO}$ electrodes after 100 cycles were presented in Figure 4d. Obviously, strong and sharp redox peaks were still observed evidently on the dQ/dV curves for the $\text{rGO/LaPO}_4/\text{LVO}$ electrode even after 100 cycles, which almost disappeared for the pristine LVO accompanied by serious capacity decay, further revealing that surface co-modification was effective to improve the reversibility of repeated lithium ion insertion/extraction in LVO cathode.

Furthermore, XRD and SEM characterization was utilized to investigate the change of crystal structure and morphology during cycling. Figure 5a shows the XRD patterns of the LVO and $\text{rGO/LaPO}_4/\text{LVO}$ electrodes before and after 100 cycles. For the cycled LVO electrode, the main diffraction peak intensity of (002) plane was rather weak, which was still maintained sharp and strong for the modified LVO electrode, suggesting the crystal structure was well-preserved upon cycling, which was primarily benefited by the effective protection of crystal structure from electrolyte corrosion by surface modification layer. Figure 5c and e shows the SEM images of the LVO and $\text{rGO/LaPO}_4/\text{LVO}$ electrodes after 100 cycles. Inevitably, cracks occurred on the LVO nanorods surface induced by the structural stress during lithiation processes, while intact nanorod surface was preserved for $\text{rGO/LaPO}_4/\text{LVO}$ electrodes even after long-term cycling as shown in Figure 5e, further verifying the improved structural stability and reversibility for the modified LVO electrode.

Based on above discussion, the interfacial schematic illustration of LVO with rGO

and LaPO_4 surface layer is schematically demonstrated in Figure 6. The LVO nanorods was distributed uniformly on the conductive rGO matrix. During discharge process, the electronic transmission between the active LVO nanorods was promoted efficiently through rGO layer which act as “bridge” to connect the adjacent LVO nanorods together. Meanwhile, the interfacial Li^+ diffusion between the bulk LVO electrode and electrolyte was also facilitated by the LaPO_4 layer, which was favorable for the excellent rate capability. Additionally, the protective layer of LaPO_4 and rGO would stabilize the electrode/electrolyte interface and protect the LVO particles from electrolyte corrosion, contributing to the improved structural stability and cyclic stability during repeated Li insertion/extraction processes.

4. Conclusions

To summarize, we successfully prepared $\text{rGO/LaPO}_4/\text{Li}_x\text{V}_2\text{O}_5$ composite electrode via chemical precipitation and frozen dryness. The $\text{rGO/LaPO}_4/\text{LVO}$ composite demonstrated significantly improved cyclic stability and rate capability. At a current density of 60 mA g^{-1} , the $\text{rGO/LaPO}_4/\text{LVO}$ electrode delivered high reversible capacity of 275.7 mAh g^{-1} with high capacity retention of 84.1% after 100 cycles. The enhanced electrochemical performance of the LVO electrode is ascribed to the promoted electronic transfer and Li^+ diffusion coefficient between active nanorods with the functionality of conductive rGO and LaPO_4 layer. The excellent electrochemical properties of $\text{rGO/LaPO}_4/\text{LVO}$ composites, together with their high specific capacity and rate capability, make tunneled lithium vanadate promising candidate for next-generation rechargeable lithium ion batteries.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version.

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Figures and Captions:

Figure 1 Crystal structure and morphology characterization. (a, b) Crystal structure of β - $\text{Li}_x\text{V}_2\text{O}_5$ with different projections along b and a -axis, respectively. V1 represent the edge-sharing VO_6 octahedra, V2 represents the corner-sharing VO_6 octahedra, and V3 represents the VO_5 pyramids. (c) XRD patterns of LVO, LaPO_4/LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$. The standard patterns of $\text{Li}_{0.33}\text{V}_2\text{O}_5$ is shown in the lower panel. (d) SEM, (e) TEM and (f) HRTEM images of LaPO_4 -coated LVO nanorods wrapped by rGO nanosheets. Inset in (e) is enlarged view of the interface.

Figure 2 XPS spectra of LVO, LaPO_4/LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$. (a) Survey spectra; (b) $\text{V}2\text{p}$; (c) core-level XPS spectra of $\text{La}3\text{d}$.

Figure 3 Electrochemical performance of LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrodes. (a) CV curves at scan rate of 0.05 mV s^{-1} . (b) Charge/discharge curves of LVO electrode. (c) Charge/discharge curves of $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrode. (d) Crystal structure of β - $\text{Li}_x\text{V}_2\text{O}_5$ with four possible tunnel sites for the inserted Li^+ in the β structure marked with different colors. (e) Cycling performance at current density of 60 mA g^{-1} . (f) Rate capability at current densities of 15 to 400 mA g^{-1} .

Figure 4 Electrochemical impedance spectrum analysis before and after 100 cycles. (a) Nyquist plots of LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrodes after initial cycles. Inset is the equivalent circuit for EIS fitting. (b) Nyquist plots of LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrodes after 100 cycles. (c) The relationship between Z' and $\omega^{-1/2}$ in the low-frequency range. (d) Differential capacity (dQ/dV) curves of LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrodes after 100 cycles.

Figure 5 Structural and morphology characterization of LVO electrode upon cycling. (a) XRD pattern with magnified patterns of the LVO and $\text{rGO}/\text{LaPO}_4/\text{LVO}$ electrodes

after 100 cycles. (b) and (c) SEM images of the LVO electrodes before and after 100 cycles. (d) and (e) SEM images of the rGO/LaPO₄/LVO electrode before and after 100 cycles.

Figure 6 The interfacial schematic diagram of LVO electrode with rGO and LaPO₄ layer, which provide effective electronic transport path and protect electrode surface from electrolyte corrosion.

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Table 1. EIS fitting data of LVO and rGO/LaPO₄/LVO after 1st and 100th cycles

Cycles	LVO	LVO	rGO/LaPO ₄ /LVO	rGO/LaPO ₄ /LVO
	R_{sei}/Ω	R_{ct}/Ω	R_{sei}/Ω	R_{ct}/Ω
1st	45.5	379.8	37.4	98.2
100th	963.2	970.2	555.8	634.5

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Supplementary Materials for

Boosting the rate and cycling performance of β - $\text{Li}_x\text{V}_2\text{O}_5$ nanorods for Li ion battery by electrode surface decoration

Pan-Pan Wang^{a,b,c}, Yue Du^{a,c}, Bao-You Zhang^b, Yan-Xin Yao^b, Yu-Chen Xiao^b, Li-Jie Ci^a,

Cheng-Yan Xu^{a,b,c,*}, Liang Zhen^{a,b,c,*}

^a School of Materials Science and Engineering, Harbin Institute of Technology (Shenzhen),
Shenzhen 518055, China

^b School of Materials Science and Engineering, Harbin Institute of Technology, Harbin
150001, China

^c MOE Key Laboratory of Micro-Systems and Micro-Structures Manufacturing, Harbin
Institute of Technology, Harbin 150080, China

E-mail: lzhen@hit.edu.cn (L.Z.); cy_xu@hit.edu.cn (C.Y.X.)

Figure S1 XRD pattern of rGO/LVO sample obtained by oven-drying.

Figure S2 EDS mapping of rGO/LaPO₄/LVO sample.

Figure S3 Raman patterns of the LVO and rGO-LaPO₄/LVO samples. The frequency mode at 143, 262, 514, 699 and 1005 cm⁻¹ are assigned to bond bending vibrations and the stretching vibrations of differing V–O bonds in β -phase bronze Li_xV₂O₅ compounds.

Figure S4 (a) Charge/discharge curves of the LVO and (b) rGO/LaPO₄/LVO electrodes at different current densities.

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