Carbon-emcoating architecture boosts lithium storage of Nb₂O₅

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ABSTRACT Intercalation transition metal oxides (ITMO) have attracted great attention as lithium-ion battery negative electrodes due to high operation safety, high capacity and rapid ion intercalation. However, the intrinsic low electron conductivity plagues the lifetime and cell performance of the ITMO negative electrode. Here we design a new carbon-emcoating architecture through single CO₂ activation treatment as demonstrated by the Nb₂O₅/C nanohybrid. Triple structure engineering of the carbon-emcoating Nb₂O₅/C nanohybrid is achieved in terms of porosity, composition, and crystallographic phase. The carbon-embedding Nb₂O₅/C nanohybrids show superior cycling and rate performance compared with the conventional carbon coating, with reversible capacity of 387 mA h g⁻¹ at 0.2 C and 92% of capacity retained after 500 cycles at 1 C. Differential electrochemical mass spectrometry (DEMS) indicates that the carbon emcoated Nb₂O₅ nanohybrids present less gas evolution than commercial lithium titanate oxide during cycling. The unique carbon-emcoating technique can be universally applied to other ITMO negative electrodes to achieve high electrochemical performance.

Keywords: niobium pentoxide/carbon nanohybrids, mesoporous, CO₂ activation, emcoating, lithium-ion battery negative electrode

INTRODUCTION

Intercalation transition metal oxides (ITMO) appeal to researchers as alternatives for negative electrodes of li-

thium-ion battery due to their high theoretical capacity, high redox potential, and low volume change [1,2]. However, intrinsic low electric conductivity restricts the rate performance and further practical application of ITMO. Great efforts on constructing nanostructured ITMO have proved that size reduction is an effective method to shorten the Li-ion diffusion length and offer better accessibility for the electrolyte [3]. However, the low electron conductivity issue remains. Compositing nanostructured ITMO with carbon matrix is a promising strategy to achieve enhanced rate performance and the carbon matrix could stabilize the ITMO nanoscale structure simultaneously during lithium ion insertion/extraction [4]. In general, carbon coating and carbon embedding are two conventional strategies to integrate ITMO with carbon [5–10]. However, the typical carbon coating tends to proceed only on the outer surface of ITMO because the carbon source can hardly access the interior region of the agglomerate. Methods such as core-shell structure construction allow enhanced carbon coating; however, convoluted process is normally involved [5]. Besides, the core-shell structure still retains individual nanoparticulate feature, which could bring adverse effects such as inferior tap density [11]. Compared with the coating method, the carbon-embedding offers continuous carbon wrapping on the total surface of ITMO [10,12,13]. Micro-/nano-scale hierarchical architectures can be built based on the embedding method. As

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a result, side effects originating from the nano-sized structure feature can be circumvented [14].

Our group has developed a new concept to embed nanoscale ITMO (NbO_2 , Nb_2O_5 , TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) in carbon matrix using dimethacrylate-based dental resin monomer as the solvent and carbon source over the past few years [15–19]. Metal ions are incorporated into the polymer network during the curing process where the dental resin monomer reacts with the ITMO precursors. Thus, super-small metal oxide nanoparticles are *in situ* generated and embedded in the carbon matrix homogeneously during the carbonization process. The as-prepared metal oxide/carbon nanohybrids present high tap density and unique electrochemical performance. However, a few critical issues remain. High content of dense structured carbon prevents the wetting of the electrolyte to access the ITMO within the carbon matrix, where electrochemical kinetics is retarded, and apparent electrochemical performance is compromised. Besides, excessive carbon matrix is generated surrounding the ITMO nanoparticle, which makes significant contribution to the overall capacity while the intrinsic electrochemical performance of ITMO is smeared [20–22]. Furthermore, the *in situ* formed carbon matrix suppresses the growth of metal oxide nanocrystal, which yields poor crystallinity and short lithiation plateau. As a result, the characteristic lithiation/delithiation profiles are deviated and the complexity of battery management is increased in practical applications.

Here, a unique emcoating concept is developed to perform carbon compositing with the nanostructured ITMO, which combines the advantages of both coating and embedding methods, while the drawbacks are avoided. Carbon emcoated Nb_2O_5 nanohybrids are constructed through facile scalable one-step carbon dioxide (CO_2) activation of the $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid with the embedding structure feature. Triple structure engineering including carbon content modification, porosity tuning, and crystallographic phase manipulation of the $\text{Nb}_2\text{O}_5/\text{C}$ emcoating nanohybrid is achieved. This strategy possesses several distinct advantages. First, excessive carbon is etched, and thin carbon coating is formed on the surface of each individual Nb_2O_5 nanoparticle, while the continuous electron conductive network remains. The shortened pathway from electrolyte to the Nb_2O_5 nanoparticle enables accelerated lithium ion diffusion, leading to enhanced electrochemical kinetics and improved rate performance. Second, the Nb_2O_5 nanoparticles are still homogeneously distributed within the micrometer-scale continuous conductive carbon matrix inherited from the

embedding structure. The agglomeration of the Nb_2O_5 nanoparticles is suppressed, where individual Nb_2O_5 nanoparticles can effectively participate in the lithiation process. Besides, the homogeneous dispersion of the Nb_2O_5 nanoparticles within the carbon matrix helps to relief mechanical stress upon lithiation, leading to improved cyclic stability. Third, compared with conventional activation methods such as hot air and KOH treatments, CO_2 activation is regarded as mild, controllable, facile, free of post-treatment, and easy to scale-up, which is particularly attractive for practical applications. Consequently, the construction of the emcoating structure within the $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid endows superior cycling stability and rate capability. Comprehensive studies on the fundamental mechanism for emcoating structure construction, phase transition of Nb_2O_5 during structure evolution, and structure-property correlation of the $\text{Nb}_2\text{O}_5/\text{C}$ emcoating nanohybrid are carried out in this study.

EXPERIMENTAL SECTION

Materials

Niobium (V) ethoxide (NbETO) was purchased from Alfa Aesar Co., Ltd. Bisphenol A-glycidyl methacrylate (Bis-GMA) and *tert*-butyl peroxy benzoate (TBPB) were obtained from Sigma-Aldrich. Poly(vinylidene fluoride) (PVDF) was donated by Solvay. Conductive carbon black (Super P) was purchased from SCM Chem, Shanghai. *N*-methyl pyrrolidone (NMP) was acquired from Aladdin Reagent Co., Ltd. All chemicals were used as received.

Sample preparation

The pristine embedding type $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrids were prepared according to our previous work with the Bis-GMA/ NbETO mass ratio of 1:1 [18]. The carbon-emcoating samples were prepared with further heat treatment at 900°C under CO_2 atmosphere with a flow rate of 0.5 L min^{-1} for 1 h. To study the mechanism responsible for the structure evolution during CO_2 heat treatment, the pristine samples were treated with CO_2 at 900°C for 2 h and 800°C for 1 and 2 h as well.

Material characterization

X-ray diffractometer (XRD; Bruker AXS D8 Advance, $\lambda = 1.5406\text{ \AA}$, 2.2 kW) was applied to identify the crystallographic phases of the niobium oxide/carbon nanohybrids and CO_2 -activated samples with 2θ from 5° to 90° . X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 XI model spec-

trometer with Al K α radiation ($h\nu = 1486.6$ eV). Scanning electron microscope (SEM; Hitachi S4800) was used to characterize the morphology at an accelerating voltage of 4 kV. The carbon content was measured by a Mettler Toledo thermogravimetric analyzer (TGA) with a temperature range from 50 to 800°C at a ramp rate of 20°C min⁻¹ in air. Phase structure of the niobium oxide/carbon nanohybrids was determined by Raman spectroscopy (Renishaw, in Via-reflex). A JEOL JEM-2100F transmission electron microscope (TEM) was adopted for high-resolution imaging and selected area electron diffraction (SAED). Specimens for TEM were prepared by sonicating the Nb₂O₅/C powders in ethanol for 10 min, which were then dropped onto a copper grid and dried by an infrared lamp. A Micromeritics ASAP2020 was applied to characterize the Brunauer-Emmett-Teller (BET) surface area and pore size distribution profile with N₂ adsorption isotherms at 77 K.

Electrochemical measurement

The electrochemical performance was evaluated using CR-2032 type coin cells in a half-cell configuration. Electrodes were prepared by manual mixing of the nanohybrid material, super P and PVDF in a mortar with a mass ratio of 8:1:1, where NMP was used as the dispersion medium. The mixture was then cast onto copper foil and dried at 80°C for 4 h. Typical electrode presented a mass density between 2 and 3 mg cm⁻². Coin cells were assembled with lithium metal foil (Dongguan Shanshan battery Materials Co., LTD) and Celgard 2400 microporous polypropylene membrane as counter electrode

and separator, respectively, in argon-filled glove box. Electrolyte from Zhangjiagang Guotai-Huarong Commercial New Material Co., LTD was adopted, with 1.0 mol L⁻¹ LiPF₆ dissolved in a solution mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and fluoroethylene carbonate (EC:DMC=1:1 by volume, FEC 5% by mass). A Neware Battery Test System was employed to conduct galvanostatic cycling and rate tests at a voltage range from 0.01 to 3.0 V (*versus* Li⁺/Li) and from 1.0 to 3.0 V (*versus* Li⁺/Li). A current rate of 1 C was set as 200 mA g⁻¹. A Solartron Analytical electrochemical workstation was used for cyclic voltammetry (CV, 0.001–3.0 V, 0.2 mV s⁻¹) and the electrochemical impedance spectroscopy (EIS, 0.001 Hz–1 MHz, 10 mV) measurements. The galvanostatic intermittent titration technique (GITT) test was carried out on a Neware Battery Test System. The battery was discharged and charged with a small pulse current at 20 mA g⁻¹ for 10 min followed by a rest period of 30 min at a potential from 0.01 to 3.0 V.

Differential electrochemical mass spectrometry (DEMS) was conducted according to previously reports [23–25]. Measurements were conducted with Swagelok type cell. Argon with a flow rate of 0.5 ml min⁻¹ was applied as conveying gas to flush out the gas generated.

RESULTS AND DISCUSSION

Fig. 1 schematically illustrates the structural evolution from embedding to emcoating of the Nb₂O₅/carbon nanohybrids through the CO₂ activation process [26,27]. The Nb₂O₅ nanoparticles of the pristine sample are fully embedded in the dense carbon matrix. With CO₂ activation

Figure 1 Schematic illustration of the Nb₂O₅/carbon nanohybrid structure evolution from embedding to emcoating.

vation, the dense carbon matrix is partially etched first, while the spatial distribution status of the Nb_2O_5 nanoparticles remains intact. CO_2 only etches the surface of carbon matrix; the inner carbon keeps its dense structure, and this carbon composition state is noted as Nb_2O_5 emcoated with dense carbon (emcoating with dense carbon, abbreviated as EDC). With further CO_2 activation, the outer surface of the Nb_2O_5 particles has no carbon coating anymore (defined as exterior region). However, the inner carbon matrix is only partially etched and thin coating layer is retained on the inner surface of the Nb_2O_5 particles (defined as interior region). This thin carbon coating on the inner surface of each Nb_2O_5 particle is connected and continuous carbon network is therefore preserved. The thin carbon coating layer tends to be porous because of extensive CO_2 activation. Thus, the sample presenting emcoating structure with thin, porous and interconnected carbon coating is fabricated (emcoating with porous carbon, abbreviated as EPC).

From a structure model perspective, both the EDC and EPC structures can be defined as following. EDC: Full carbon coating particles inter-connected by dense carbon matrix. Within this structure, any two arbitrary points at the surface of the Nb_2O_5 particle can be connected by at least one route throughout the carbon matrix. In actual material systems, tremendous amount of points at the particle surface are connected by at least one route throughout the carbon matrix. The particles are fully covered by carbon, which are further connected by carbon matrix. Because the carbon matrix is not etched, it retains a dense structure. EPC: Partial carbon coating particles inter-connected by porous carbon matrix. In actual material systems, the carbon coating at the surface of the particles is partially removed, leaving part of the particle surface naked. Meanwhile, the carbon matrix of inter-connecting neighbouring particles becomes porous due to partial carbon removal. Exterior region of the EPC: Carbon-free region on the surface of the particles within the EPC. Inside this specific region, any two arbitrary points at the surface of the Nb_2O_5 particles cannot be connected by a route throughout the carbon matrix. In actual material systems, this region may have some small areas still covered by residual carbon. However, it is generally defined as the exterior region of the EPC for the reason of simplicity. Interior region of the EPC: Carbon remaining region within the EPC. In this specific region, there are at least two points at the surface of the Nb_2O_5 particles connected by at least one route throughout the carbon matrix. However, in actual material systems, tremendous amount of points are connected by at least one

route throughout the carbon matrix.

Compared with the pristine embedding structure, the emcoating structure bears a good conductivity with less carbon content. Additionally, the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid provides enhanced accessibility towards electrolyte and shorter Li-ion transportation path for Nb_2O_5 nanoparticles than the EDC structure as interpreted by the sketch in Fig. 1.

Coral structured Nb_2O_5 will be generated by further enhanced CO_2 activation with extended time or elevated temperature (for example, at 900°C), where carbon matrix is fully eliminated, and naked Nb_2O_5 nanoparticles start to agglomerate. Carbon coating can be further formed onto the coral Nb_2O_5 by different methods such as chemical vapor deposition (CVD) and mechanical ball-milling. However, the carbon coating can only proceed at the outer surface of the coral structured Nb_2O_5 , where the interior region is difficult to be coated. It is impossible to build the emcoating structure *via* CO_2 activation treatment of the carbon-coated coral Nb_2O_5 particulate agglomerate. Electron conductivity improvement from carbon coating is not as efficient as that from the emcoating structure.

The actual structure evolution of the $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid from embedding to emcoating induced by CO_2 activation is characterized by SEM and TEM (Fig. 2 and Fig. S1). The pristine carbon-embedded Nb_2O_5 nanohybrids present a dense bulk structure with a smooth surface, particle size ranging from 1 to $5\ \mu\text{m}$ (Fig. 2a-1). Upon CO_2 activation at 800°C , the Nb_2O_5 nanoparticles grow from 5 nm (Fig. 2a-2) to 20–50 nm (Fig. 2b-2). High-resolution TEM (HRTEM) and SAED images show a clear phase transition from hexagonal phase in the pristine (Fig. 2a-3, a-4) to the orthorhombic phase (Fig. 2b-3, b-4). The surface of the EDC structured $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid becomes porous and rough with some nanoparticles exposed at the surface due to consumption of carbon by CO_2 (Fig. 2b-1). It proves that only slight surface activation occurs at 800°C , consistent with previously reported papers [28–31]. After further treatment at 900°C , small pores are generated at the surface of the EPC structured Nb_2O_5 (Fig. 2c-1). A bimodal particle size distribution is observed with the EPC structured Nb_2O_5 , which are 15–20 nm and 50–100 nm, respectively (Fig. 2c-2). HRTEM images (Fig. 2c-3, c-4) confirm that the small crystal refers to the orthorhombic Nb_2O_5 and the large one refers to the monoclinic Nb_2O_5 . In addition, the EPC sample shows more porous structure inside the carbon matrix, consistent with the surface morphology revealed by the SEM images. With further activation time,

Figure 2 Structure evolution of the $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid from pristine Nb_2O_5 embedded with carbon (a) to emcoated with dense carbon (EDC, activated at 800°C for 2 h) (b), and to emcoated with porous carbon (EPC, activated at 900°C for 1 h) (c) induced by the CO_2 activation. Image details: SEM (a-1, b-1, and c-1), TEM (a-2, b-2, and c-2), HRTEM (a-3, b-3, c-3, and c-4), and SAED (a-4, b-4, and c-5). Insets in a-1, b-1, and c-1: low magnification SEM images of the $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrids.

coral structured Nb_2O_5 is presented (Fig. S1a-1). The grain size grows to 100 nm and the crystallographic phase is fully transferred to the monoclinic Nb_2O_5 (Fig. S1b), confirmed by the diffraction patterns from the SAED result. The microscopic structure characterization illustrates that the carbon matrix evolves from dense bulk to porous and interconnected structure due to CO_2 activation, while the spatial distribution of the Nb_2O_5 nanoparticles remains intact within the carbon matrix.

To further gain insights about the interior carbon distribution of the emcoating structure, a simulation model was established to estimate surface area contribution proportion from different regions of the Nb_2O_5 nanoparticulate agglomerate (Fig. 3). Based on the actual size revealed by the microscopic images, the nanoparticulate agglomerate is approximated as a cube with a length of 5.5 μm , built by packing the nanoparticles with a diameter of 7.8 nm. The simulation model demonstrates that the inner surface provided by the particles contributes more than 99.7% of the total surface area; while the outer surface area accounts for only 0.3% of the total surface area. The simulation results suggest that the emcoating

Figure 3 Simulation model of the nanoparticulate powder for inner and outer surface area distribution estimation. Grey cube: bulk shape of the Nb_2O_5 nanoparticulate agglomerate. Black sphere: inside part of the Nb_2O_5 particles. Blue sphere: outside part of the Nb_2O_5 particles. Red sphere: Nb_2O_5 particles on the edge of cube.

strategy enables carbon coating on the majority of the surface area of the nanoparticulate agglomerate. While the conventional carbon coating can only coat the outer

surface area, which is only a tiny portion of the total surface area. Compared with the conventional surface coating method, the emcoating strategy holds a great potential to improve the electrochemical kinetics and rate capability by coating carbon onto the inner surface of the nanoparticulate agglomerate.

Carbon contents of the Nb₂O₅/C nanohybrids were determined by thermo gravimetric analyzer (TGA). Fig. 4a and Fig. S2a indicate that the carbon content decreases when the structure changes from embedding to emcoating after the CO₂ activation. In addition, both

increasing activation temperature and elongated activation time reduce the carbon content: the carbon etching process at 900°C is much stronger than that at 800°C and the carbon component is fully removed when the sample is processed at 900°C for 2 h. To be precise, the pristine embedding type Nb₂O₅/C nanohybrid presents the carbon content of 40%, while the carbon contents of the EDC, EPC and coral Nb₂O₅ are 27%, 8% and 0%, respectively (Table S1). Both the pristine and CO₂-activated samples present characteristic peaks of disordered carbon (D-band) at 1360 cm⁻¹ and graphitic carbon (G-band) at

Figure 4 Structure characterizations of the Nb₂O₅/C nanohybrids with carbon embedding (pristine), EDC, and EPC. Thermogravimetric profiles (a) and Raman spectroscopy (b) of the pristine, embedded, and emcoated Nb₂O₅; N₂ adsorption/desorption isotherms (inset: corresponding Barrett-Joyner-Halenda (BJH) pore size distribution curves) of the pristine embedded Nb₂O₅ (c), EDC structured Nb₂O₅/C (d), EPC structured Nb₂O₅/C (e) and coral Nb₂O₅ (f).

1590 cm^{-1} in the Raman spectra (Fig. 4b). Although the coral structured Nb_2O_5 displays no carbon content from the TGA result, trace amount of carbon contributes to the characteristic peaks (Fig. S2b). The integrative intensity ratio of the D band and the G band (I_D/I_G) refers to the extent of disordered carbon (Table S1). The I_D/I_G value decreases with increasing activation temperature, which indicates higher graphitization after activation [32,33]. In addition, with activation under 900°C, small peaks appear at fingerprints region, and the coral structured Nb_2O_5 bears strong peaks at 118, 261, 632 and 992 cm^{-1} originating from the Nb_2O_5 phase [34]. The increasing peak intensity of the Nb_2O_5 is assigned to the particle growth and enhanced crystallization, consistent with the TEM images [35].

BET measurements investigated the porosity evolution of the $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrids along with different CO_2 activation treatments (Fig. 4c–f). The pristine carbon-embedded Nb_2O_5 presents type I adsorption/desorption isotherms, referring to a microporous structure (Fig. 4c). After CO_2 activation, typical type IV isotherms are observed in the EDC and EPC structured Nb_2O_5 , and the pore size distribution shifts to 3.8 nm (EPC structured Nb_2O_5) and 20 nm (EDC structured Nb_2O_5), confirming the presence of mesoporous structure (Fig. 4d, e) [36]. Note that CO_2 activation would generate micropores on the surface of carbon matrix, and thus slight pore size increase is detected [28,29]. The coral Nb_2O_5 possesses the type II isotherms with a non-porous structure (Fig. S2d). As the porous structure is mostly contributed by the carbon content in the nanohybrid, the pores vanish due to full removal of the carbon component by CO_2 . Assisted by the strong pore generation effect of CO_2 activation under 900°C, the EPC structured Nb_2O_5 presents a substantial increase of BET surface area from 57.7 to 221 $\text{m}^2 \text{g}^{-1}$ (Table S2). While the EDC structured Nb_2O_5 shows only a minor increase of the surface area due to less extent of the CO_2 activation at a low temperature.

XRD was applied to investigate the crystallographic phase change of the $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrids induced by the CO_2 activation (Fig. 5a, b). Compared with the pristine carbon embedding $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid, the diffraction peaks of both the EDC and EPC samples become sharper, showing enhanced crystallization of the Nb_2O_5 nanoparticles through the CO_2 activation process, consistent with the TEM results. In addition, different crystallographic phases are observed with the CO_2 activation at 800 and 900°C. The pristine carbon embedding $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid presents a typical hexagonal phase (JCPDS No. 28-0317) (Fig. 5a); while the EDC structured $\text{Nb}_2\text{O}_5/\text{C}$

shows a splitting peak at 28°, implying a transformation from hexagonal phase to orthorhombic phase (JCPDS No. 27-1003). When the activation temperature increases to 900°C, the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ presents further phase transition from pure hexagonal phase to bi-phase of orthorhombic/monoclinic (Fig. 5b) with the quantities of the orthorhombic and monoclinic of 43.1% and 56.9%, respectively, based on a reference intensity ratio (RIR) method [37]. Generally, the phase transition of Nb_2O_5 from hexagonal to monoclinic depends on the annealing temperature (Table 1). Although the pristine sample is synthesized at 900°C, the dense-structured carbon matrix can introduce carbon doping into the Nb_2O_5 nanoparticles, which hinders the phase transition from hexagonal to orthorhombic/monoclinic under 900°C. Such obstruction effect by the doped carbon has been revealed in the TiO_2 phase transition [38–41]. During the CO_2 activation process, the carbon matrix is etched gradually, which partially eliminates the doped carbon and facilitates phase transition.

In order to understand the mechanism governing the phase transition of Nb_2O_5 induced by the CO_2 activation, XPS was applied to detect the valence state and chemical environment of the Nb_2O_5 nanoparticles. The XPS spectra (Fig. 5d–f and Fig. S3) confirm the existence of carbon, oxide and niobium on the surface of the $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid. Peaks assigned to the binding energies of 287.5 and 288.5 eV are observed in the high resolution C 1s XPS spectra, which originate from the carbonate species [42,43]. The existence of these peaks indicates that the Nb_2O_5 nanoparticles are doped with C^{4+} . Apart from the C 1s spectra, the O 1s spectra present a peak located at around 532 eV, which is ascribed to the carbonate species as well [44]. Table S3 shows that the pristine embedding $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid presents the highest content of carbonate species, which inhibits the phase transition of the Nb_2O_5 nanoparticle. Thus, the phase transition is precluded at 900°C and the Nb_2O_5 nanoparticles remain as hexagonal phase. With carbon consumption through the CO_2 activation process, the amount of the carbonate species decreases as indicated by the XPS spectra. The restriction effect of the carbon doping on the phase transition is weakened, where the phase transition from hexagonal to orthorhombic and monoclinic is observed.

Based on the comprehensive structure analyses of the $\text{Nb}_2\text{O}_5/\text{carbon}$ nanohybrids, the mechanism of the phase transition induced by the CO_2 activation process is interpreted. The hexagonal phase of Nb_2O_5 is normally only stable in the temperature range from 500 to 600°C, while phase transition tends to occur at elevated temperatures

Figure 5 XRD patterns of the pristine carbon embedded Nb₂O₅/C and carbon emcoated (both EDC and EPC) Nb₂O₅/C nanohybrids (a, b). XPS survey (c) and high-resolution O 1s (d), C 1s (e) and Nb 3d (f) of the EPC structured Nb₂O₅/C nanohybrid.

Table 1 Relationship between heat-treatment temperature and crystallographic phase of Nb₂O₅ [45]

Temperature (°C)	Crystallographic phase
500–600	Hexagonal
600–800	Orthorhombic
900	Monoclinic

[45,46]. However, the existence of dense carbon coating and carbon doping precludes the phase transition and the

hexagonal phase is retained at 900°C in this study. When activated by CO₂, the carbon species is etched, alleviating the mechanical stress and reducing the amount of the doped carbon simultaneously. As a result, the energy barrier for the phase transition is lowered, where the transition from hexagonal to orthorhombic and monoclinic phase occurs [47]. The phase transition from hexagonal phase to orthorhombic and further monoclinic phase is triggered with either extended time range or elevated temperature of the CO₂ activation treatment.

It is noted that, according to our previous studies, Nb_2O_5 would be reduced to NbO_2 through Equations (1) and (2), which is generated from the residual amount of CO_2 in the tube furnace [18]. While, in this study, under CO_2 atmosphere, the abundant CO_2 pushes the reaction of Equation (2) towards the left direction. Thus, Nb_2O_5 will not be reduced to NbO_2 .

The electrochemical performances of the CO_2 -activated $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrids were tested using CR-2032 coin type half-cells. Fig. 6a and Fig. S4 exhibit the CV curves of the activated samples at 0.2 mV s^{-1} with voltage range from 0.005 to 3.0 V. No obvious redox peak is observed in the pristine carbon embedding $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid due to poor crystallization of the Nb_2O_5 component. After

CO_2 activation, the EDC structured $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid shows redox couple of $\text{Nb}^{4+}/\text{Nb}^{5+}$ at 1.84/1.62 V, referring to the delithiation/lithiation process of the orthorhombic Nb_2O_5 [48,49]. The EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid and coral Nb_2O_5 present three redox pairs at 2.2/2.0 V, 1.8/1.6 V and 1.25/1.17 V, which are assigned to the lithium ion de-intercalation/intercalation process of the monoclinic Nb_2O_5 . In addition, a small peak appears at 1.0–1.2 V in the first cycle, indicating the formation of solid electrolyte interphase (SEI) [50].

Charge and discharge profiles of the CO_2 -activated $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrids are displayed with a voltage range of 0.01–3.0 V at a current density of 40 mA g^{-1} (Fig. 6b and Fig. S5). Apart from a small sloping plateau originating from the SEI formation process, no obvious plateau is observed in the first discharging cycle of the pristine carbon embedding $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid

Figure 6 Electrochemical performance of the pristine carbon embedding $\text{Nb}_2\text{O}_5/\text{C}$ and carbon emcoating $\text{Nb}_2\text{O}_5/\text{C}$ ($1 \text{ C}=200 \text{ mA g}^{-1}$): charge/discharge profiles (a) and CV curves (b) of the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$; cycling (c) and rate (d) performances of the pristine carbon embedding $\text{Nb}_2\text{O}_5/\text{C}$ and carbon emcoating $\text{Nb}_2\text{O}_5/\text{C}$ with the voltage range of 0.01–3.0 V; cycling (e), rate (f), and long cycling performance at 200 mA g^{-1} (g) with the cut-off voltage from 1.0 to 3.0 V.

(Fig. S5a). After the CO₂ activation at 800°C with an enhanced crystallization, a small plateau appears at 1.5 V on discharge and 1.8 V on charge, consistent with the CV results (Fig. S5b). When the activation temperature increases to 900°C, multiple plateaus between 1.0 and 2.0 V are shown in the EPC structured Nb₂O₅/C nanohybrid and coral Nb₂O₅ samples (Fig. 6b, Fig. S5c). The main plateau at 1.6 V refers the sharp redox pair at 1.8/1.6 V in the CV profiles, which further confirms the charge/discharge behaviors of the monoclinic Nb₂O₅. The pristine carbon embedding Nb₂O₅/C, EDC structured Nb₂O₅/C, EPC structured Nb₂O₅/C and coral Nb₂O₅ deliver initial discharge/charge capacities of 535/192, 689/274, 750/396 and 468/345 mA h g⁻¹, corresponding to initial coulombic efficiencies (ICE) of 35.9%, 39.8%, 52.8% and 73.7%, respectively. The large irreversible capacity is ascribed to the intrinsic properties of resin-induced hard carbon and the formation of SEI on the surface of carbon matrix [50]. Thus, the ICE is improved after the CO₂ activation process due to the decreased carbon content.

Cycling performance of the Nb₂O₅/C nanohybrids was measured at a current density of 40 mA g⁻¹ (Fig. 6c). The EDC structured Nb₂O₅/C also presents improved cycling performance than the pristine sample, while the coral Nb₂O₅ shows poor reversibility in 50 cycles. The total removal of the carbon matrix by CO₂ activation deteriorates the overall electron conductivity of the electrode and lack of carbon matrix makes it difficult to buffer the mechanical stress generated upon lithiation, which tends to accelerate capacity decay. The EPC structured Nb₂O₅/C shows the best performance, presenting a discharge capacity of 387 mA h g⁻¹ after 200 cycles, which is nearly twice that of the pristine and other activated samples. It is worth noting that the specific capacity of the EPC structured Nb₂O₅/C is much higher than the theoretical value of Nb₂O₅ (ca. 200 mA h g⁻¹), where the excessive lithium-ion storage is likely from the surface storage mechanism because of the increased surface area [51–53]. The CO₂-activated Nb₂O₅ nanohybrids present improved rate performance at various current densities of 0.1 to 5 C, and the reversed current density of 0.1 C (Fig. 6d). The EPC structured Nb₂O₅ delivers a specific capacity of 169 mA h g⁻¹ at 5 C, corresponding with capacity retention of 37.6% with respect to the capacity at 0.1 C. In order to further investigate the cycling and rate performance, correlative measurements were conducted at the voltage window of 1.0–3.0 V. Fig. 6e shows that the EPC structured Nb₂O₅ remains a specific capacity of 184 mA h g⁻¹ after 200 cycles, which retains 88% of the initial capacity. The specific capacity is nearly 5 times that

of the pristine carbon-embedded Nb₂O₅ (42 mA h g⁻¹ after 40 cycles). The improved electrochemical performance at a reduced voltage window is due to enhanced crystallization of the Nb₂O₅ nanoparticles by CO₂ activation. Regarding the rate performance, the EPC structured Nb₂O₅ presents capacity retentions of 99%, 93%, 89%, 79% and 62% at current densities of 0.2, 0.5, 1, 2 and 5 C (Fig. 6f). It is noted that coral Nb₂O₅ could not deliver comparable performances to the EPC structured Nb₂O₅ even coated with effective carbon matrix (Fig. S6), illustrating superior ion transportation in the EPC structure than conventional carbon coating. Fig. 6g demonstrates the cycling stability of the EPC structured Nb₂O₅, delivering a capacity of 173 mA h g⁻¹ after 500 cycles at 1 C. Both the cycling and rate performance of the Nb₂O₅/C nanohybrid is significantly improved by the emcoating technique, and to the best of our knowledge, the cycling performance of the EPC structured Nb₂O₅ is superior to the reported studies in both cut-off voltage ranges of 0.01–3 V and 1.0–3.0 V (Table 2).

To reveal the mechanism governing the high rate performance of the EPC structured Nb₂O₅, kinetics-related tests were carried out to determine the specific capacity contributions from the diffusion-controlled and capacitive processes [59]. Fig. 7a presents the CV measurements of the EPC structured Nb₂O₅ and pristine carbon embedding sample with scan rates from 0.2 to 1.2 mV s⁻¹ and the strong redox peak pair at 1.5 V refers to the delithiation/lithiation of Nb₂O₅. With increasing scan rates, the redox peaks tend to be broad and shift to high voltage due to polarization. The cathodic peak is marked as Peak 1, representing the lithium insertion process. According to Randles Sevcik equation, the peak current (*I_p*, A) from

Table 2 Electrochemical performance of the reported Nb₂O₅-based negative electrodes

Electrode	Potential range (V)	Gravimetric capacity (mA h g ⁻¹)	Current density (mA g ⁻¹)	Ref.
NbO ₂ /C	0.01–3.0	225 (500 th)	200	[18]
NbO _x @C	0.01–3.0	298 (100 th)	100	[54]
Nb ₂ O ₅ /C	0.01–3.0	385 (100 th)	100	[55]
Nb ₂ O ₅ capsule	0–3	421 (100 th)	100	[56]
Vein-like Nb ₂ O ₅	1.0–3.0	201 (50 th)	200	[49]
Nb ₂ O ₅ /CNTS	1.0–3.0	168 (500 th)	100	[56]
Nb ₂ O ₅ /NbO ₂	1.0–3.0	123 (900 th)	200	[57]
Nb ₂ O ₅	1.2–3.0	140 (200 th)	100	[58]
Nb ₂ O ₅ /C	0.01–3.0	387 (200 th)	40	This work
	1.0–3.0	184 (500 th)	200

Figure 7 Kinetics analyses of the lithium ion storage mechanism of the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$. Details: CV profiles at various scan rates (a); relationship between the peak current and scan rate in logarithmic format (b); capacitive contribution at a scan rate of 0.2 mV s^{-1} (c); contribution ratio of the capacitive and diffusion-controlled capacities at various scan rates (d). GITT analyses of the EPC structured Nb_2O_5 . Details: GITT profiles of the discharge/charge process (e); single step of the GITT curves (f); linear fit of E versus $\tau^{1/2}$ for a typical titration (g); apparent lithium diffusion coefficient (D_{Li}) of the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ calculated from the GITT profiles (h). Additionally, the EIS results (Fig. S8) confirm the improved diffusion behavior from the unique carbon structure as well.

the CV scans can be applied to estimate the lithium diffusion coefficient, D_{Li}^+ ($\text{cm}^2 \text{s}^{-1}$) [60]:

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} C. \quad (3)$$

According to Randles Sevcik equation, the lithium diffusion coefficients of the EPC structured Nb_2O_5 and pristine carbon embedding Nb_2O_5 are estimated as 4.3×10^{-11} and $7.3 \times 10^{-13} \text{cm}^2 \text{s}^{-1}$, respectively (Fig. S7).

In addition, the contribution of the capacitance process can be analyzed by the equation below:

$$i = av^b, \quad (4)$$

where i stands for the peak current, a and b are adjustable constants [61,62]. The a and b values are empirical parameters, which can be calculated by fitting the $\log(v)$ - $\log(i)$ plot (Fig. 7b). Note that the b value indicates the contribution of diffusion-controlled process and surface capacitance process. When the b value is close to 1, it represents a surface-controlled intercalation process. While the b value is close to 0.5, a diffusion-controlled process is dominating [61]. From the slope of $\log(v)$ - $\log(i)$, the b values of cathodic (peak 1) and anodic (peak 2) are 0.68 and 0.78, respectively, which illustrates a surface-controlled process of the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$. In addition, the contribution of the diffusion process and capacitance process can be extracted from the following equation:

$$i = k_1 v + k_2 v^{1/2}, \quad (5)$$

where $k_1 v$ stands for the contribution of the surface capacitance and $k_2 v^{1/2}$ stands for the contribution of the diffusion-controlled process. Fig. 7c, d depict that the proportion of capacitance contribution is 48.6% at the scan rate of 0.2mV s^{-1} . With increasing scan rates to 1.2mV s^{-1} , the proportion rises to 70.0%. Thus, the majority of the lithium storage of the EPC structured Nb_2O_5 originates from the capacitive behavior, which conduces to the excellent high rate performance.

GITT experiment was applied to investigate the lithium ion diffusion coefficient of the EPC structured Nb_2O_5 . The cell was cycled at 0.1 C to reach stabilized cycling performances before measurement. Fig. 7e shows the data for the GITT analysis during the discharge/charge process. The apparent D_{Li}^+ can be estimated based on the equation derived from Fick's second law [63–65]:

$$D_{\text{Li}} = \frac{4}{\pi} \left(\frac{m_B V_m}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\tau (dE_\tau / d\sqrt{\tau})} \right)^2, \tau \ll \frac{L^2}{D_{\text{Li}}}, \quad (6)$$

where m_B , M_B and V_m are the real mass, molar mass and molar volume of the active material, respectively. S is the area of the electrode and τ is the current pulse time. ΔE_τ is

the potential change caused by pulse current in a single-step GITT experiment and ΔE_s is transient potential change after eliminating the IR drop, which can be extracted from Fig. 7f. From Fig. 7g, it can be extracted that E and $\tau^{1/2}$ present linear relationship during single titration. Thus, Equation (6) can be simplified as follow [63–65]:

$$D_{\text{Li}} = \frac{4}{\pi \tau} \left(\frac{m_B V_m}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2, \tau \ll \frac{L^2}{D_{\text{Li}}}. \quad (7)$$

D_{Li^+} of the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ during de-lithiation/lithiation process is calculated ranging from 10^{-10} to $10^{-18} \text{cm}^2 \text{s}^{-1}$ (Fig. 7h). The lithium diffusion coefficient calculated from GITT matches well with the results from the CV analysis, which further confirms the rapid lithium ion diffusion behavior of the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid.

The improved electrochemical performance of the EPC structured Nb_2O_5 is attributed to the unique structure from the effect of CO_2 activation process. The crystal phase of the Nb_2O_5 component is modified and crystallization is also enhanced. With increasing crystallinity, lithiation plateau is prolonged. Besides, the bulk structure is tuned from embedding to interconnected and mesoporous carbon emcoating structure after CO_2 activation, and the contact area between electrolyte and electrode is increased and the diffusion path is largely shortened, which facilitate the electron and ion transport. Compared with conventional coating structure, the interconnected carbon matrix provides more carbon composition on the surface of the Nb_2O_5 nanoparticles. In addition, re-constructed surface and increase of surface area enhance lithium-ion storage capability due to the additional surface lithium storage process for the CO_2 -activated $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrids.

The intercalation negative electrode was implicated with gassing problems, which hampers the practical application [23,66]. The gassing behavior of the EPC structured Nb_2O_5 electrode was explored with differential electrochemical mass spectrometry (DEMS) (Fig. 8a). Gas species with molecular weights of 44, 30, 28, and 2 were monitored to characterize CO_2 , C_2H_6 , C_2H_4 and H_2 , respectively. Commercial lithium titanate (LTO) was applied as the control sample (Fig. 8b). The gas evolution profiles for the first galvanostatic discharge/charge cycles at 0.1 C are presented. During the discharge process, different from LTO, gas evolution of C_2H_4 and C_2H_6 is observed, which could be attributed to the reduction of EC and DMC [23,67,68]. The origination of H_2 during discharge is assigned to the reduction of trace water from

Figure 8 DEMS patterns with initial discharge/charge cycle of the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ (a) and commercial LTO electrode (b).

the electrode [69]. Nevertheless, as the feature gas of the LTO electrode from the reduction of Ti^{4+} to Ti^{3+} , CO_2 is only observed in the LTO electrode [70]. After integration, the specific gas amounts of the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid and LTO are calculated as 2.47 and 3.04 μmol , implying that the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid exhibits a reduced gas evolution behavior than the commercial LTO electrode.

CONCLUSIONS

In summary, $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid with the carbon-emcoating architecture was constructed through CO_2 activation treatment of the $\text{Nb}_2\text{O}_5/\text{C}$ sample with the Nb_2O_5 nanoparticles embedded in the carbon matrix. Triple structure engineering of the carbon-emcoated $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid is achieved by the CO_2 activation process, where the content and microstructure of the carbon matrix, and crystallographic phase of the Nb_2O_5 are well tuned. Compared with the typical carbon-coating and carbon-embedding structure, dominant interior surface of the Nb_2O_5 nanoparticulate agglomerate is covered by the continuous porous carbon within the carbon-emcoated $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid. Superior electrochemical performance is exhibited by the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid with a discharging capacity of 387 mA h g^{-1} over 200 cycles. With the narrowed voltage window of 1.0–3.0 V, a capacity of 173 mA h g^{-1} is maintained after 500 cycles. The D_{Li^+} of the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid shows two order of magnitude higher than that of non-activated samples. The DEMS profile indicates that the EPC structured $\text{Nb}_2\text{O}_5/\text{C}$ nanohybrid exhibits reduced gassing behavior compared with the commercial

lithium titanate counterpart. The paper provides a facile method and fundamental understanding about construction of the carbon-emcoating architecture towards high-performance energy storage materials.

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通过构筑嵌覆型碳结构提升 Nb_2O_5 的储锂性能

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摘要 嵌入型过渡金属氧化物因具有安全的工作电压、高比容量和快速的嵌锂能力而受到广泛关注。但低本征电导率特性严重影响其作为锂电负极材料的寿命和性能。本文通过简便易行、可规模化放大的二氧化碳热处理方法构筑了具有新型嵌覆型碳结构的 $\text{Nb}_2\text{O}_5/\text{C}$ 纳米杂化材料。在控制碳含量的前提下, 实现了颗粒聚集体内部表面可控碳包覆。以嵌覆型碳结构的 $\text{Nb}_2\text{O}_5/\text{C}$ 纳米杂化材料为负极组装的锂离子电池在 40 mA g^{-1} 电流密度下容量可达 387 mA h g^{-1} , 而在 200 mA g^{-1} 电流密度下循环500次后, 容量保持率在92%以上。采用电化学滴定、差分电化学质谱(DEMS)等方法对嵌覆型五氧化二铌/碳纳米杂化材料脱嵌锂动力学过程以及产气行为进行了研究。本文提出的嵌覆型碳结构有望为高性能嵌入型过渡金属氧化物的结构设计提供参考。