

Carbide-Derived Niobium Pentoxide with Enhanced Charge Storage Capacity for Use as a Lithium-Ion Battery Electrode

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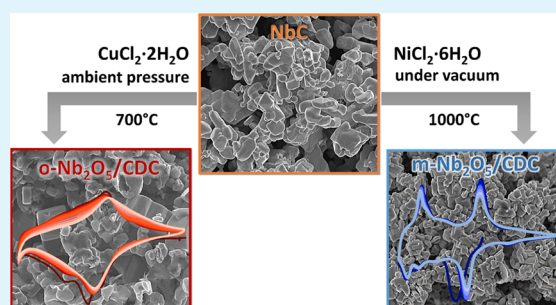
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ABSTRACT: Nb_2O_5 has been explored as a promising anode material for use as lithium-ion batteries (LIBs), but depending on the crystal structure, the specific capacity was always reported to be usually around or below 200 mAh/g. For the first time, we present coarse-grained Nb_2O_5 materials that significantly overcome this capacity limitation with the promise of enabling high power applications. Our work introduces coarse-grained carbide-derived Nb_2O_5 phases obtained either by a one-step or a two-step bulk conversion process. By in situ production of chlorine gas from metal chloride salt at ambient pressure, we obtain in just one step directly orthorhombic Nb_2O_5 alongside carbide-derived carbon (o- $\text{Nb}_2\text{O}_5/\text{CDC}$). In situ formation of chlorine gas from metal chloride salt under vacuum conditions yields CDC covering the remaining carbide core, which can be transformed into metal oxides covered by a carbon shell upon thermal treatment in CO_2 gas. The two-step process yielded a mixed-phase tetragonal and monoclinic Nb_2O_5 with CDC (m- $\text{Nb}_2\text{O}_5/\text{CDC}$). Our combined diffraction and spectroscopic data confirm that carbide-derived Nb_2O_5 materials show disordering of the crystallographic planes caused by oxygen deficiency in the structural units and, in the case of m- $\text{Nb}_2\text{O}_5/\text{CDC}$, severe stacking faults. This defect engineering allows access to a very high specific capacity exceeding the two-electron transfer process of conventional Nb_2O_5 . The charge storage capacities of the resulting m- $\text{Nb}_2\text{O}_5/\text{CDC}$ and o- $\text{Nb}_2\text{O}_5/\text{CDC}$ are, in both cases, around 300 mAh/g at a specific current of 10 mA/g, thereby, the values are significantly higher than that of the state-of-the-art for Nb_2O_5 as a LIB anode. Carbide-derived Nb_2O_5 materials also show robust cycling stability over 500 cycles with capacity fading only 24% for the sample m- $\text{Nb}_2\text{O}_5/\text{CDC}$ and 28% for o- $\text{Nb}_2\text{O}_5/\text{CDC}$, suggesting low degree of expansion/compaction during lithiation and delithiation.

KEYWORDS: lithium-ion battery, electrochemical energy storage, hybrid material, carbide-derived oxide, niobium pentoxide



1. INTRODUCTION

Electrochemical energy storage (EES) with high specific energy and power is essential for the successful transition of combustion engine vehicles to electric cars, advanced mobile communication devices, and energy harvesting technologies.^{1,2} The most advanced and widespread type of EES is the lithium-ion battery (LIB)³ because of its long cycle life, high energy density, and efficiency.⁴ To meet the growing demands in energy and power ratings, there is a constant need for the development of improved and optimized LIB electrode materials. Metallic lithium offers a high theoretical capacity of 3860 mAh/g with a low redox potential of -3.04 V vs. standard hydrogen electrode (SHE) but is plagued by dendrite formation and safety concerns; therefore, lithium insertion compounds are preferred for rechargeable LIBs.^{4,5} Graphite, for example, provides a high specific capacity of 372 mAh/g and a low insertion potential of $+0.2$ V vs. Li/Li^+ , which translates to a high energy and power density.¹ However, graphite suffers from large stress during Li insertion/desertion, resulting in reduced cycling stability.⁶ As an alternative, researchers have explored TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$

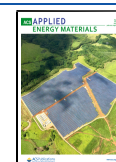
(LTO), which have a high operating voltage of 1.7 and 1.5 V vs. Li/Li^+ , respectively. While there is the benefit of a low volume change for TiO_2 (4%) and LTO (<1%), these two materials provide only a limited theoretical capacity of about 170 mAh/g.^{7,8}

Niobium pentoxide (Nb_2O_5) is an alternative insertion-type anode to LIBs due to its various superior features.⁹ The operating redox potential of Nb_2O_5 is above 1 V vs. Li/Li^+ .¹⁰ At this voltage, electroplating is prevented, and a safer device operation is enabled.¹¹ Nb_2O_5 can be obtained in different crystal structures, including hexagonal, orthorhombic, tetragonal, and monoclinic, which have different electrochemical properties.^{12,13} For example, Viet et al. measured for the

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pseudohexagonal Nb₂O₅ electrode a specific capacity of 150 mAh/g at redox couple peaks of 1.84 V vs. Li/Li⁺, while Li et al. showed for polymorph Nb₂O₅ a specific capacity of 190 mAh/g within the voltage window of 1.2–3.0 V vs. Li/Li⁺.^{14,15} Hollow nanospheres of hexagonal Nb₂O₅ exhibit a specific capacity of 172 mAh/g at a C-rate of 0.5.¹⁶ Pseudohexagonal and orthorhombic Nb₂O₅/amorphous carbon core/shell materials provide about 200 mAh/g at 0.1 C in the voltage range of 1.0–3.0 V vs. Li/Li⁺.¹⁷ 3D holey-graphene/orthorhombic Nb₂O₅ has been found to exhibit a capacity of 139 mAh/g at a high C-rate of 10.¹⁸ Nanobelts composed of orthorhombic Nb₂O₅ found by Wei et al. presented an initial specific capacity of 250 mAh/g in the voltage range of 1.2–3.0 V vs. Li/Li⁺.¹⁹ Tetragonal Nb₂O₅ was described as a transformation phase in orthorhombic and monoclinic phases, where the initial specific capacity was ca. 230 mAh/g in the voltage window of 1.2–3 V vs. Li/Li⁺.¹³ Using electrospinning, our team reported reversible capacities of 160 and 240 mAh/g, respectively, for tetragonal and monoclinic Nb₂O₅/carbon fiber mats at a specific current of 0.025 A/g in the voltage window of 0.8–3.0 V vs. Li/Li⁺.²⁰ In all these structures, orthorhombic and tetragonal Nb₂O₅ are highly promising candidates due to the fact that they are capable of maintaining their original structures even after lithium insertion, resulting in better electrochemical cycling performance.^{13,21} The orthorhombic Nb₂O₅ phase shows suppressed lithiation/delithiation peaks in the electrochemical signature with more pseudocapacitive resemblance as a result of ion insertion into the large interstitial sites.^{22,23} Monoclinic Nb₂O₅ was reported to have the highest capacity among them of 242 mAh/g.¹⁴

Until now, different crystal structures of Nb₂O₅ have been mostly reported to yield a lithiation capacity of about 200 mAh/g, which aligns with a two-electron transport process via the transition between Nb⁵⁺ and Nb⁴⁺ and the formation of Li₂Nb₂O₅.^{24,25} Kumagai et al.²¹ have mentioned already in 1983 that Nb₂O₅ should allow insertion of “at least” two lithium ions. Furthermore, Shi et al.²⁴ speculated about the concurrence of Nb⁵⁺ to Nb⁴⁺ and the Nb³⁺ oxidation state changes during lithiation/delithiation. This uncertainty about the upper limit for reversible Li-insertion into Nb₂O₅ host structures for LIBs has inspired our work. There have also been two recent studies, where an excess value of 200 mAh/g was enabled by utilization of nanoscaled Nb₂O₅ and the added surface area may play a key role in enhancing the energy storage metrics.^{26,27} Our work, however, targets to unlock the high charge storage domain not by nanoscale material design but by defect engineering and crystal structure optimization of bulk materials (starting with coarse-grained carbide particles as the precursor). Controlling the structural defects (stacking faults and oxygen vacancies) not only significantly boosts the conductivity of materials but also enables a higher intrinsic charge storage capacity.^{28,29}

Our work uses the unique tool of carbide-derived oxide synthesis to design Nb₂O₅ with tailored defect structures and implement carbon at the nanoscale level to make it an advanced hybrid electrode material. We introduce, for the first time, cyclic stable bulk Nb₂O₅ with a reversible high specific capacity of 300 mAh/g. This high performance is observed for carbide-derived Nb₂O₅/carbon hybrid materials with a disordered crystal structure. We present data with this high charge storage capacity for two Nb₂O₅ crystal structures, namely orthorhombic Nb₂O₅, and mixed monoclinic and tetragonal Nb₂O₅. Carbides are a convenient and versatile precursor for the synthesis of metal oxides and metal oxide/carbon hybrids. We used two synthesis routes: a two-step and a one-step method. Facile carbide

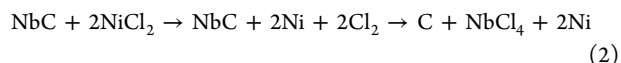
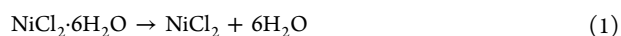
conversion can be obtained by the two-step process of chlorination (to create carbon) followed by oxidation (to create the metal oxide phase but without removing all formerly formed carbon).³⁰ Alternatively, one-step processing of metal carbide via chloroxidation triggered by the decomposition of a chloride hydrate (e.g., NiCl₂·6H₂O) directly leads to the coexistence of metal oxide and carbide.³¹

2. EXPERIMENTAL

2.1. Material Synthesis. 2.1.1. Nb₂O₅ Material Nomenclature.

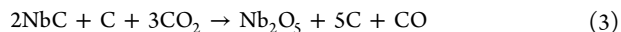
Considering the specific crystal structures of m-Nb₂O₅/CDC and o-Nb₂O₅/CDC, our nomenclature deviates from previous studies.³² For example, the conventional name for orthorhombic Nb₂O₅ would be Tief-Nb₂O₅ (T-Nb₂O₅).³³ We prefer to address our material as o-Nb₂O₅ as a more suitable name considering the differences in the crystal structure compared to actual Tief-Nb₂O₅. Also, we chose m-Nb₂O₅ with *m* standing for *mixed* because it contains tetragonal Mittel-Nb₂O₅ (M-Nb₂O₅) and monoclinic Nadel-Nb₂O₅ (N-Nb₂O₅). We also used commercially available Nb₂O₅, which contains tetragonal and monoclinic phase contents and is labeled com-Nb₂O₅.

2.1.2. Synthesis of m-Nb₂O₅/CDC. The synthesis of m-Nb₂O₅/CDC was performed by two thermal treatment steps. In the first step, for the synthesis of NbC/CDC particles, in situ production of chlorine under vacuum conditions was used for the reactive extraction of niobium from NbC using NiCl₂·6H₂O as the chlorine source.³⁴ At this step, the decomposition of NiCl₂·6H₂O under vacuum conditions leads to incomplete conversion of NbC (eqs 1 and 2). The following step is to oxidize the residual NbC with CO₂ instead of using O₂ to avoid complete carbon burn-off.

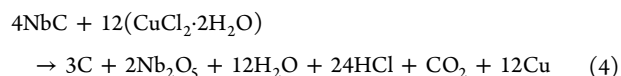


For the incomplete conversion of NbC to carbide-derived carbon (CDC), NbC (H.C. Starck, purity ≥98%) and NiCl₂·6H₂O (Alfa Aesar, purity 98%) were homogenized using a mortar with a stoichiometric ratio of 1.0 mol NbC per 0.8 mol NiCl₂·6H₂O. Then, the solid mixture was transferred into a graphite crucible, and the latter was placed in the isothermal zone of a tubular furnace (Gero, type: DZF 100–750/13, diameter: 34 cm, and length: 1.5 m). Afterward, the furnace was evacuated until a pressure of about 1 mbar was achieved, heated to 1000 °C at a rate of 3.3 °C/min, and held at 1000 °C for 3 h. The furnace was then cooled to room temperature. The sample from the furnace was washed with 200 mL of aqueous 3 M HCl to eliminate elemental Ni. After stirring the solution overnight, the particles were filtered by using an excessive amount of distilled water. The filtered particles were dried at 75 °C overnight. The obtained sample was labeled as NbC/CDC.

In the second step of the synthesis, the NbC/CDC particles were subjected to carbide-to-oxide conversion. The thermal treatment was carried out using a VG Scientia GP-CVD tube furnace in a gas mixture of Ar (flow rate: 100 cm³/min) and CO₂ (flow rate: 50 cm³/min) at 900 °C for 1 h. During the heating and cooling process, the CO₂ gas flow was excluded. The sample was labeled m-Nb₂O₅/CDC. The process can be expressed by eq3.



2.1.3. Synthesis of o-Nb₂O₅/CDC. The synthesis of o-Nb₂O₅/CDC involved the one-step chloroxidation of niobium carbide (NbC, H. C. Starck, purity ≥98%) and CuCl₂·2H₂O (Sigma Aldrich, purity ≥98%) with a stoichiometric amount of 1.0 mol NbC per 4.0 mol CuCl₂·2H₂O under ambient pressure.³¹ The process can be expressed by eq4.



NbC and CuCl₂·2H₂O were ground using a mortar until a homogeneous mixture was obtained. The obtained mixture was transferred to a quartz glass crucible and placed in an isothermal

zone of a quartz tube furnace (HTRH, Gero). After sealing the furnace, Ar gas was flushed at a flow rate of 50 cm³/min during the whole process. As a first step, the furnace was held at room temperature for 5 h to equilibrate the Ar gas atmosphere. Then, the furnace was heated to 700 °C at a rate of 2.5 °C/min and held at 700 °C for 3 h. Afterward, the furnace was cooled to room temperature. The obtained material was then poured into 200 mL of 3 M HCl solution and stirred overnight to remove elemental Cu. The acquired solution was filtered by using the vacuum filtration method with an excess amount of distilled water until the pH of the filtrate reached a value of 7. The filtrated product was dried at 75 °C overnight. The resulting sample was labeled o-Nb₂O₅/CDC.

2.2. Material Characterization. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM 7500F field emission scanning electron microscope at an accelerating voltage of 3 kV. All samples were placed on a steel sample holder by using carbon tape. Transmission electron microscope (TEM) images were recorded using a JEOL JEM-2100F system operating at 200 kV in a vacuum. The samples were prepared by dispersing and sonicating in isopropanol and drop-cast onto a copper grid with a lacey carbon film. In addition, the elemental composition mapping of m-Nb₂O₅/CDC and o-Nb₂O₅/CDC was performed by energy-dispersive X-ray analysis (EDX) using an X-Max-150 detector from Oxford Instruments coupled with a JEOL JEM-2100F system.

Elemental analysis (CHNS) was carried out using a Vario Micro Cube System with sulfanilamide as the calibrant and a reduction temperature of 850 °C. Quantitative analysis of elemental oxygen was performed by using an OXY cube oxygen analyzer at 1450 °C.

X-ray photoelectron spectroscopy (XPS) was conducted using an Axis Ultra DLD spectrometer (Kratos Analytical) with monochromatic Al-K α as the photoelectron excitation source. At an X-ray radiation power of 150 W (15 kV, 10 mA) with a spot size of about 250 μ m, we used pass energies of 160 eV (wide scan) and 80 eV (elemental scan). For high-resolution scans, we used an X-ray radiation power of 225 W and a pass energy of 10 eV.

Powder X-ray diffraction (XRD) was performed using a Bruker AXS D8 Advance diffractometer with Ni-filtered Cu-K α radiation (wavelength: 0.15406 nm, voltage: 40 kV, current: 40 mA) for the powder samples of o-Nb₂O₅/CDC, m-Nb₂O₅/CDC, and com-Nb₂O₅. A variable diverge slit was used at the primary beam side and a Bruker AXS LYNXEYE detector at the secondary beam side. The background was reduced by discriminating against the detector. Air scattering was reduced by a knife edge. Measurements were carried out with standard powder sample holders in the 2 θ range between 7 and 150° with a step size of 0.013° and a total scan time of 4 h.

X-ray powder diffraction of NbC/CDC was carried out using a Bruker AXS D8 Discover diffractometer with Cu-K α radiation (wavelength: 0.15406 nm, voltage: 40 kV, current: 40 mA), a Goebel mirror (point focus: 0.5 mm), and a Bruker AXS VANTEC 500 area detector. The measurement was performed by positioning the detector from 20 to 100° 2 θ with an increment of 20° 2 θ . The total measurement time was chosen as 55 min. The Bruker AXS software TOPAS 5 was used for Rietveld refinements for all the powder samples. Instrumental line broadening was included in a fundamental parameter approach.³⁵

Raman spectra were recorded using a Renishaw inVia system equipped with an Nd-YAG laser (532 nm) and a power of 0.5 mW at the surface of the samples. From each of the samples, 10 different spots were recorded with five accumulations and 30 s acquisition time in the range of 100–3200 cm⁻¹. Peak analysis was performed by baseline corrections, assuming Voigt peak profiles for D-mode, G-mode, D'-mode, and amorphous carbon.

To obtain values for the specific surface area (SSA) and pore volume of the samples, nitrogen gas sorption analysis (GSA) at -196 °C was performed using a Quantachrome Quadrasorb system. The samples were degassed at 300 °C under vacuum conditions for 24 h. The total pore volume was obtained at a relative pressure value of 0.95. The SSA values were calculated using the Brunauer–Emmett–Teller (BET) equation (Ref.³⁶) in the linear pressure range of 0.01–0.1 (Ref.³⁷) using the ASiQwin software package.

Thermogravimetric analysis (TGA) using a TG 209 F1 Libra system (Netzsch) was performed to characterize oxidation vacancies of the m-Nb₂O₅/CDC and o-Nb₂O₅/CDC samples. TGA of the samples was carried out in a mixture of synthetic air (80 cm³/min) and Ar (20 cm³/min) with a heating rate of 5 °C/min.

2.3. Electrochemical Characterization. A slurry of the electrodes was prepared using a mixture of 80 mass % of active materials (o-Nb₂O₅/CDC, m-Nb₂O₅/CDC, and com-Nb₂O₅), 10 mass % of polyvinylidene fluoride (PVdF, Alfa Aesar) as a binder, and 10 mass % of carbon black (C65, Imerys Graphite & Carbon) as a conductive additive. The required amount of active materials and carbon black was mixed using a mortar. The mixtures were added into a solution of PVdF and *N*-methyl-2-pyrrolidone (NMP, Sigma-Aldrich). An excess amount of NMP was added to the slurry to adjust the viscosity, and the resulting slurry was stirred overnight, and then coated on Cu foil with a wet thickness of 125 μ m. The coated electrodes were dried at 110 °C in a vacuum for 10 h. After that, the coated electrodes were gently pressed in a rolling machine (HR01 hot rolling machine, MTI) and cut into a circle shape with a diameter of 12 mm. The average mass loading values of o-Nb₂O₅/CDC and m-Nb₂O₅/CDC were 2.1 and 1.4 mg/cm², respectively.

Coin cells (2032-type) were assembled in an argon-filled glove box (O₂, H₂O < 1 ppm) with lithium foil (diameter of 12 mm) as the counter and reference electrode, two pieces of Celgard 2325 (diameter of 18 mm) as a separator, and 1 M lithium hexafluorophosphate (LiPF₆) in an ethylene carbonate (EC) and dimethyl carbonate (DMC) mixture in the volumetric ratio of 1:1-EC:DMC (Sigma-Aldrich) as the electrolyte.

A VMP300 system connected to a Bio-Logic multichannel potentiostat was used to record the cyclic voltammetry (CV) results in the potential range of 1.0–2.5 V vs. Li/Li⁺ at a scan rate of 0.05 mV/s. For galvanostatic charge/discharge cycling with potential limitation, GCPL measurements were carried out using an Arbin Battery Cycler in the range of 1.0–2.5 V vs. Li/Li⁺ using 0.01–10 A/g to observe the rate capability and specific current of 1 A/g to examine cyclic stability. The specific capacity was calculated based on the mass of the active material of the electrodes.

To quantify the strain of the electrodes during charging and discharging, electrochemical dilatometry measurements were carried out using an ECD-2-nanosystem from EL-CELL connected to a VSP300 Bio-Logic multichannel potentiostat.³⁸ The dilatometer cell was assembled in an Argon-filled glove box (O₂, H₂O < 1 ppm) with metallic lithium (diameter of 11 mm) as the counter and reference electrode, one piece of glass microfiber filters (GF/F, Whatman) with a diameter of 13 mm as an additional separator, and 1 M lithium hexafluorophosphate (LiPF₆) in an ethylene carbonate (EC) and dimethyl carbonate (DMC) mixture in the volumetric ratio of 1:1-EC:DMC (Sigma Aldrich) as the electrolyte. The measurements were performed at a scan rate of 0.5 mV/s at 25 $\pm$ 1 °C.

3. RESULTS AND DISCUSSION

3.1. Material Characterization. To better capitalize on the charge storage capacity intrinsic to ion insertion into the host matrix of crystalline niobium pentoxide, we designed a synthesis strategy to implement electrically conductive carbon at the nanoscale level within the metal oxide matrix.³⁹ Such hybrids are attractive electrode materials for combined high power and high energy applications.^{39–41} For our work, we used two different synthesis routes: (1) a two-step process first incompletely converted NbC to CDC at 1000 °C yielding NbC/CDC; then, the residual core was subjected to thermal treatment in CO₂ at 900 °C to oxidize the carbide core without completely removing the CDC phase, yielding mixed monoclinic and tetragonal niobium pentoxide/carbide-derived carbon (m-Nb₂O₅/CDC). (2) The one-step chloroxidation of NbC at 700 °C yielded orthorhombic niobium pentoxide/carbide-derived carbon (o-Nb₂O₅/CDC). To better understand the influence of the structural defect on the electrochemical properties of m-Nb₂O₅/

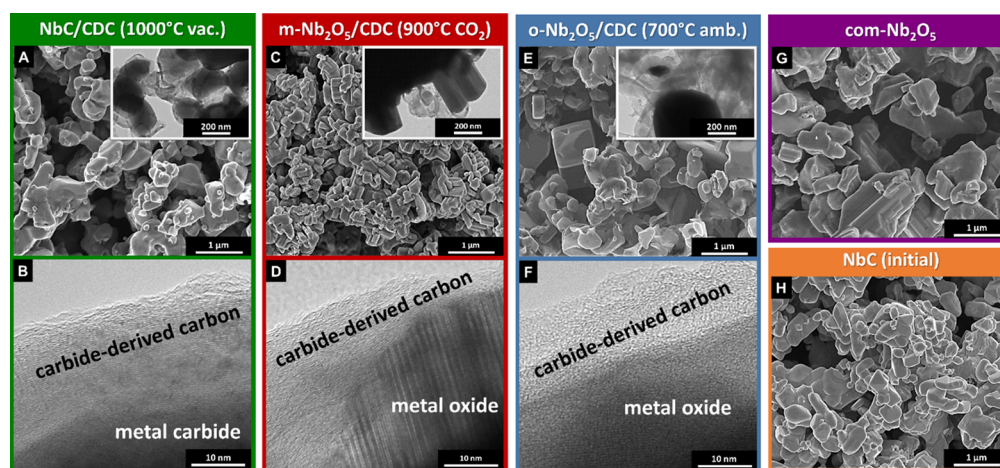


Figure 1. Scanning electron micrographs and TEM micrographs (inset, upper right corner) (A, B) of the NbC/CDC, (C, D) of m-Nb₂O₅/CDC, (E, F) of o-Nb₂O₅/CDC. Scanning electron micrograph of (G) com-Nb₂O₅ and (H) the initial NbC powder.

CDC, we further investigated commercial niobium pentoxide (com-Nb₂O₅), which also contains a monoclinic and tetragonal Nb₂O₅ phase mixture with a lower degree of defect.

In our two-step synthesis, scanning electron micrographs show that the NbC/CDC material is composed of particles in the range of ca. 0.5–1 μm (Figure 1A). This value aligns with the initial particle size of the NbC material (Figure 1H) as the carbide-to-CDC transformation is known to be largely conformal, that is, preserves the size and shape of the initial ceramic.^{42,43} Transmission electron micrographs (Figure 1A,B) reveal the presence of carbon (CDC) predominantly at the outer regions of the NbC granules. The CDC domains are partially removed but not completely lost after oxidation at 900 °C in CO₂, as indicated by the decreased particle size with a rod-like morphology (Figure 1C,D). Thereby, the m-Nb₂O₅/CDC sample qualifies as a hybrid material of carbon (2.6 mass %) and niobium oxide (97.4 mass %), as confirmed by chemical analysis (Table 1).

Table 1. Elemental Composition Analysis by XPS and Carbon Content Measured by Elemental CHNS-O Analysis

sample	XPS		CHNS-O	
	Nb:O atomic ratio	Nb (at%)	C (mass %)	O (mass %)
m-Nb ₂ O ₅ /CDC	0.36	15.2	2.6 ± 0.1	12.5 ± 0.7
o-Nb ₂ O ₅ /CDC	0.24	5.2	5.7 ± 0.3	29.6 ± 1.6
stoichiometric Nb ₂ O ₅	0.40	28.6	0	30.1

As seen in Figure 1E, the particle morphology and the size of o-Nb₂O₅/CDC are very close to the initial NbC material (Figure 1H). In comparison to m-Nb₂O₅/CDC, o-Nb₂O₅/CDC shows a much more disordered carbon phase as a result of the lower synthesis temperature.⁴² Chemical analysis shows 5.7 mass % of carbon and 94.3 mass % of niobium pentoxide (Table 1), yielding, like for m-Nb₂O₅/CDC, a hybrid material of carbon and metal oxide.

The structure of the NbC/CDC particles was further analyzed by XRD. The diffraction pattern was refined using Rietveld refinement (Supplementary Information, Figure S1 and Table S1). We determined residual cubic (*Fm*3*m*) NbC with a lattice parameter of *a* = 0.45 nm with the characteristic Bragg positions at 34.7, 40.3, 58.3, and 69.6° 2θ. After oxidation in CO₂, NbC/

CDC was converted to m-Nb₂O₅/CDC, and the corresponding diffractogram did not match with common Nb₂O₅ phases (Figure 2A).

Based on X-ray diffraction, the most likely explanation for the measured intensities found for m-Nb₂O₅/CDC (Figure 2A) and com-Nb₂O₅/CDC (Figure 2D) was to assume the co-existence of the two different crystal phases of Nb₂O₅. To this end, we calculated the diffraction patterns of monoclinic Nb₂O_{4.91} (space group *P2*/*m*, ICSD 160156; Figure 2B)⁴⁴ and tetragonal Nb₂O₅ (space group *I4*/*mmm*, ICSD 17027; Figure 2C).⁴⁵ By comparing the calculated and measured intensities in Figure 2A and Figure 2D, we see a fair and partial matching to the powder pattern; no reasonable agreement between the calculated and observed patterns was achieved when assuming only one crystal structure (i.e., either only tetragonal or only monoclinic).

The calculated position of the (330) reflection of the tetragonal phase at 18.6° 2θ was shifted to higher angles compared to the observed one. In contrast, the calculated (440) reflection at 24.8° 2θ was shifted to lower angles. This may not be compensated by variations of the lattice parameters. Either another structure type of lower symmetry or special properties of the microstructure of the tetragonal phase might cause this phenomenon. A similar problem was encountered in the case of the monoclinic phase. The reflection groups around 18 and 25° 2θ would have to move toward another, which was not possible in the given symmetry.

As seen in Figure 2B,C, tetragonal Nb₂O₅ (M-Nb₂O₅) and monoclinic Nb₂O₅ (N-Nb₂O₅) are structurally closely related. These structures are composed of blocks of linked NbO₆ octahedra with different block sizes and shearing of these blocks.^{45–47} The defects of oxygen in Nb₂O_{4.91} are compensated by forming a shear structure of the tetragonal Nb₂O₅. An even more drastic splitting of the reflections may be found in the pattern of orthorhombic Nb₂O_{4.83} (space group *Cmcm*, ICSD 160157, Ref.⁴⁴). The reflection splitting of Nb₂O₅ correlates with the oxygen content.⁴⁴ This means that a smaller number of oxygen deficiencies translate to a lower reflection splitting.

Severe anisotropic reflection broadening is present in the diffraction patterns of the sample m-Nb₂O₅/CDC (Figure 2A). The (00*L*) reflections show only minor broadening, while (*hk*0) reflections show major broadening. A lattice parameter very similar to *c* in tetragonal Nb₂O₅ is also given by both other

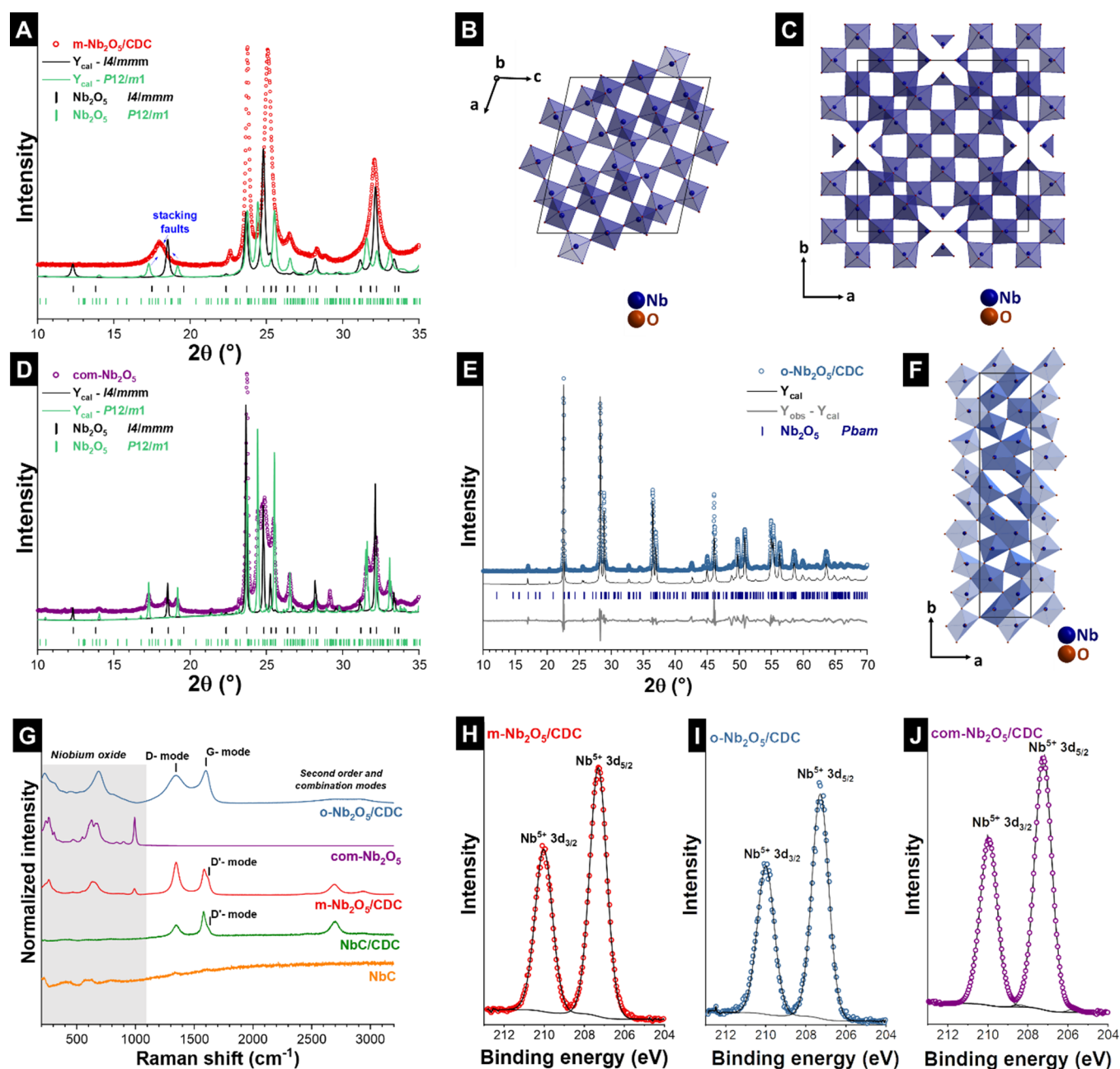


Figure 2. (A) Measured X-ray diffraction pattern of m-Nb₂O₅/CDC with the calculated pattern of monoclinic Nb₂O_{4.91} (P12/m1) and tetragonal Nb₂O₅ (I4/mmm). (B) Calculated crystal structure of monoclinic Nb₂O_{4.91} (P12/m1) and (C) tetragonal Nb₂O₅ (I4/mmm). (D) Measured X-ray diffraction pattern of com-Nb₂O₅ with the calculated pattern of monoclinic Nb₂O_{4.91} (P12/m1) and tetragonal Nb₂O₅ (I4/mmm). (E) Rietveld refinement of the X-ray diffraction pattern of o-Nb₂O₅/CDC. (F) Calculated crystal structure of orthorhombic Nb₂O₅ (Pbam). (G) Raman spectra and (H–J) XPS Nb 3d spectra of the samples.

structures (ca. 0.382 nm), while the other lattice parameters are different and range from 2.03 nm in the tetragonal structure to 1.57 and 1.79 nm in the monoclinic structure. Different arrangements of the shearing structures may coexist within small domains, without disrupting the mean symmetry of the host lattice completely. This leads to diffuse broadening instead of distinct sharp reflections. Also, stacking faults have been reported to exist within Nb₂O₅ samples.⁴⁷ Stacking faults may cause symmetry contradictory shifting of reflections and isotropic or anisotropic or even asymmetric broadening.^{48–50} Therefore, the observed pattern is consistent with tetragonal Nb₂O₅ as the host lattice with different types of domain defects, a combination of different shear structures and stacking faults.

Therefore, the overall structure may be described as defect-rich tetragonal.

We included in our study also commercially available Nb₂O₅ (com-Nb₂O₅). The analysis of com-Nb₂O₅ (Figure 2D) showed partial fitting with fixed microstructural parameters using the phases of Nb₂O_{4.91} (space group P2/m) and tetragonal Nb₂O₅ (space group I4/mmm). The reflections of com-Nb₂O₅ (especially at 17.5/18.5/19.1 °2θ) display a lower degree of broadening and less shifting in comparison with the reflections of m-Nb₂O₅/CDC (Figure 2A). A lower reflection splitting correlates with oxygen vacancies in the structures. The reflection splitting of m-Nb₂O₅/CDC is much higher than that of com-Nb₂O₅. Hence, the m-Nb₂O₅/CDC material possesses higher

oxygen deficiency than com-Nb₂O₅. Therefore, the com-Nb₂O₅ can be characterized as a lower-degree-defected mixed monoclinic and tetragonal state structure.

The X-ray diffractogram of o-Nb₂O₅/CDC (Figure 2E) can be well fitted using the orthorhombic structure of Nb₂O₅ proposed by Kato et al. (space group *Phm*, ICSD 1840).³³ Four of the seven sites of Nb were originally described with *x,y,z* sites (Wyckoff position 8i, multiplicity 8) with *z* being close to 1/2, leading to a split position with a site occupancy factor (SOF) of 0.5. The additional three 4g Nb sites with SOF < 0.1 were defined to fit the residual electron density. An R-value *R_{wp}* of 8.27% was achieved using this model in Rietveld refinement. To simplify the model, the three 4g Nb sites were removed, and the former 8i Nb sites were substituted by *x,y,1/2* sites (Wyckoff position 4h, multiplicity 4) with a value of SOF = 1. Using the simplified model, we obtained a value for *R_{wp}* of 8.64%. Since the difference in the residuals was small and the simplified model provided an adequate description of the pattern, we used it in our work, and the corresponding crystal structure is shown in Figure 2F and Supporting Information, Table S1. The reflection profile of o-Nb₂O₅/CDC also reveals a minor but slightly anisotropic broadening of the reflections. Especially the (001) reflection at 22.6° 2θ and the (002) reflection at 46.1° 2θ show a sharper reflection profile compared to other reflections. Such is consistent with the lattice strain, and additional weak reflections may relate to a small amount of the secondary phase, like a different structure of niobium with lower symmetry.

For further characterization, we employed Raman spectroscopy (Figure 2G). The Raman spectra of NbC/CDC, m-Nb₂O₅/CDC, and o-Nb₂O₅/CDC show the characteristic peaks of incomplete graphitic carbon for sp²-hybridized carbon, D- and G-modes at around 1346 and 1588 cm⁻¹, and carbon-related combination and overtone modes between 2500 and 3200 cm⁻¹.⁵¹ The samples NbC/CDC and m-Nb₂O₅/CDC present also a D'-mode at 1632 cm⁻¹, which is related to a disorder-induced splitting of the carbon E_{2g} mode.⁵² The presence of a discernable D'-mode aligns with edge-defects in a carbon network with a higher degree of graphitic ordering compared to m-Nb₂O₅/CDC. In the latter case, we see much broader D- and G-mode bands.

The peak deconvolution of the Raman spectra is outlined in Table 2 and Supplementary Information, Figure S2. The full-

Table 2. Raman Spectra Analysis of the Carbon D- and G-Modes^a

sample	mode	position (cm ⁻¹)	FWHM (cm ⁻¹)	I _D /I _G
NbC/CDC	D-mode	1346	73 ± 7	0.9 ± 0.2
	G-mode	1580	37 ± 5	
m-Nb ₂ O ₅ /CDC	D-mode	1348	63 ± 4	1.4 ± 0.2
	G-mode	1584	56 ± 2	
o-Nb ₂ O ₅ /CDC	D-mode	1344	164 ± 7	2.7 ± 0.5
	G-mode	1601	68 ± 3	

^aFWHM = full-width at half-maximum.

width at half maximum (FWHM) of the D- and G-mode of o-Nb₂O₅/CDC was 164 ± 7 and 68 ± 3 cm⁻¹, respectively. For comparison, for NbC/CDC, the D-mode FWHM was 73 ± 7 cm⁻¹ and the G-mode FWHM was 37 ± 5 cm⁻¹. The narrower D- and G-modes align with the lower I_D/I_G ratio of NbC/CDC (0.9 ± 0.2) compared to o-Nb₂O₅/CDC (1.4 ± 0.2). This can be explained by the partial oxidation of the CDC when

transforming NbC/CDC into m-Nb₂O₅/CDC. Even broader D-mode (164 ± 07 cm⁻¹) and G-mode (68 ± 3 cm⁻¹) along with a larger I_D/I_G ratio (2.7 ± 0.5) were seen for o-Nb₂O₅/CDC. The more disordered nature of the carbon in o-Nb₂O₅/CDC was a result of the lower processing temperature (700 °C) compared to m-Nb₂O₅/CDC (900–1000 °C) as well known from conventional CDC synthesis.^{53–55} In addition to the disordered structure, the CDC present in m-Nb₂O₅/CDC and o-Nb₂O₅/CDC is also nanoporous, as seen from the enhanced specific surface area of 19 and 57 m²/g, respectively (Supplementary Information, Table S2; sorption isotherm are displayed in Supplementary Information, Figure S3).

Raman spectra of m-Nb₂O₅/CDC and o-Nb₂O₅/CDC also show vibrational modes related to Nb–O–Nb in the low wavenumber region of 100–300 cm⁻¹ and the Nb–O stretching mode in the range of 500–800 cm⁻¹.⁵⁶ While the edge-shared octahedral NbO₆ stretching mode of o-Nb₂O₅/CDC displays the Raman peak at 688 cm⁻¹, m-Nb₂O₅/CDC shows the Raman peak at 628 cm⁻¹.⁵⁷ The latter peak indicates distorted NbO₆ octahedra in the structure of o-Nb₂O₅/CDC, while the Raman peak of m-Nb₂O₅/CDC located at 688 cm⁻¹ aligns with the more ordered NbO₆ octahedra.^{56,58} We also find the spectral feature of the Nb=O terminal double bond in the region of 850–1000 cm⁻¹ for m-Nb₂O₅/CDC and o-Nb₂O₅/CDC samples.⁵⁶ In addition to that, the Raman spectrum of com-Nb₂O₅ (Figure 2G) shows only niobium oxide peaks in the region of 100–1000 cm⁻¹.

X-ray photoelectron spectroscopy (XPS) was performed to further analyze the Nb-valence states of o-Nb₂O₅/CDC, m-Nb₂O₅/CDC, and com-Nb₂O₅. The XPS spectra of Nb 3d of the samples are shown in Figure 2H–J. The identical binding energy for Nb 3d (Nb⁵⁺) in Nb₂O₅ was detected at 210.1 and 207.3 eV for Nb 3d_{5/2} and Nb 3d_{3/2}, respectively.⁵⁹ The O 1 s-signal was fitted to three subpeaks located at 530.3, 531.7, and 532.9 eV, which were attributed to the Nb–O bond, C–O bond/hydroxyl groups, and H₂O/C=O, respectively (Supplementary Information, Figure S4A–C).¹⁴ As seen from Table 1, the measured Nb:O atomic ratio of m-Nb₂O₅/CDC (0.36) and o-Nb₂O₅/CDC (0.24) was both lower than what was expected for stoichiometric Nb₂O₅ (0.4). The closest value to the stoichiometrically ideal ratio was found for com-Nb₂O₅ (0.39), as seen in Supplementary Information, Table S3. In addition, we further performed thermogravimetric analysis of m-Nb₂O₅/CDC and o-Nb₂O₅/CDC using a mixture of synthetic air and argon (Supporting Information, Figure S5). The observed mass gain (Table 1) aligns with oxygen deficiency in m-Nb₂O₅/CDC (~4%) and o-Nb₂O₅/CDC (~1%). Carbon is mostly present in the sp²-hybridization, but we also find sp³-carbon, C–O bonds, and COO groups with the XPS peaks at 284.1, 285.1, 286.6, and 288.7 eV, respectively (Supplementary Information, Figure S4D,E).^{60,61}

3.2. Electrochemical Analysis. Initial electrochemical testing showed the need to add a conductive additive (carbon black; 10 mass %) to the Nb₂O₅/carbon hybrid material to fully capitalize on the intrinsic charge storage capacity of the samples. The intrinsically present carbon (CDC) provides better charge transport in the samples; however, an insufficient amount of carbon is present in the samples as the sole charge carrier conductor. We first carried out cyclic voltammetry at a scan rate of 0.05 mV/s, and the cut-off potential was between 1.0 and 2.5 V vs. Li/Li⁺ (Figure 3A–C). The cyclic voltammogram of m-Nb₂O₅/CDC shows sharp reduction peaks at 1.6 and 1.1 V vs. Li/Li⁺ and oxidation peaks at 1.2 and 1.7 V vs. Li/Li⁺. The

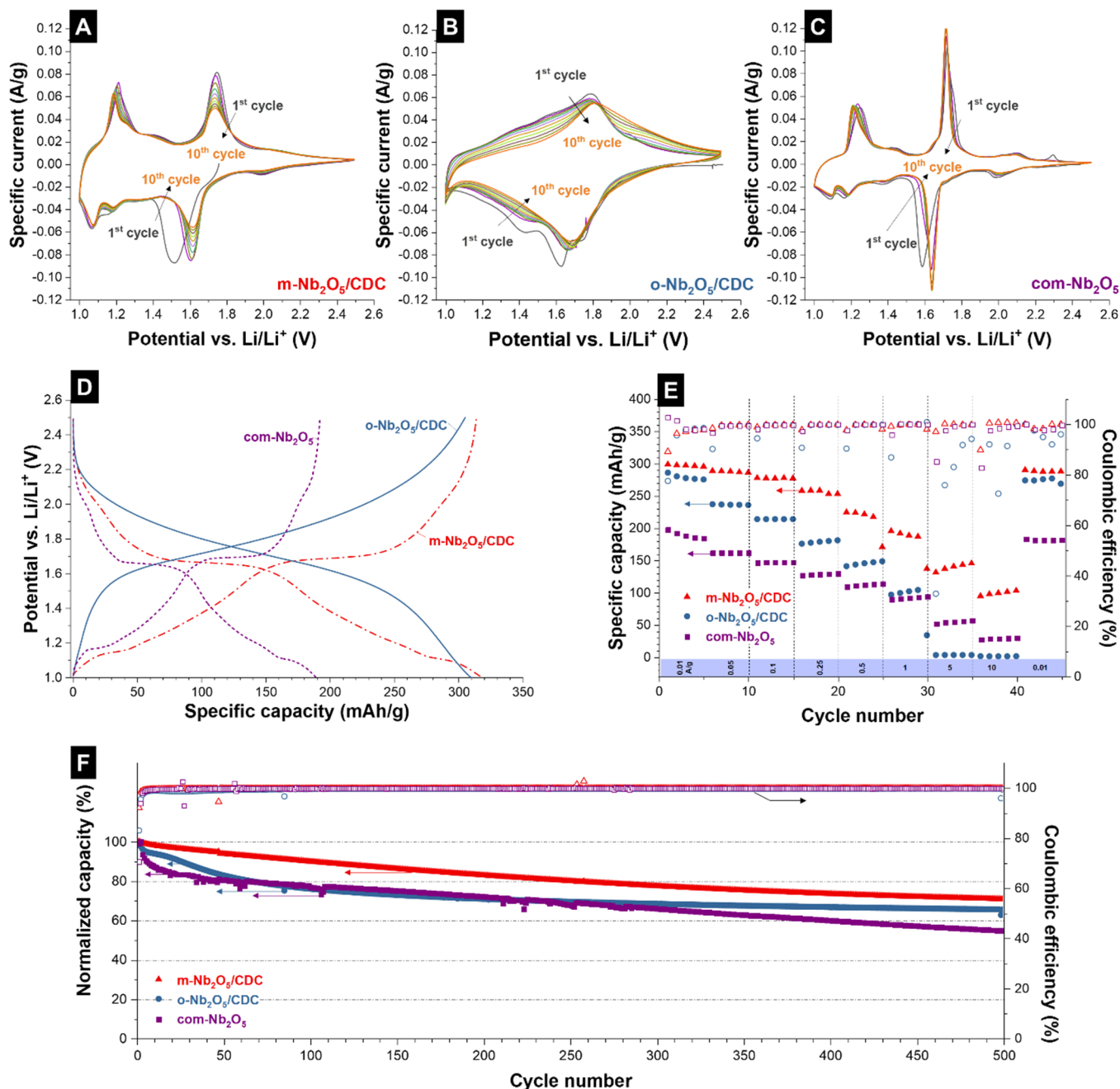


Figure 3. Cyclic voltammograms of (A) m-Nb₂O₅/CDC, (B) o-Nb₂O₅/CDC, and (C) com-Nb₂O₅. GCPL charge/discharge profiles of (D) m-Nb₂O₅/CDC, o-Nb₂O₅/CDC, and com-Nb₂O₅ samples at a specific current of 0.01 A/g. Rate handling performance of (E) m-Nb₂O₅/CDC, and o-Nb₂O₅/CDC. Cyclic stability performance of (F) m-Nb₂O₅/CDC, o-Nb₂O₅/CDC, and com-Nb₂O₅ at a specific current of 0.1 A/g.

amplitude of the redox peak pair at 1.6 V vs. Li/Li⁺ and 1.7 V vs. Li/Li⁺ seen in the cyclic voltammograms is decreased as the number of cycles is increased, while the oxidation peak at 1.2 V vs. Li/Li⁺ is increased (Figure 3A). The cyclic voltammogram of o-Nb₂O₅/CDC shows just one broad lithiation/delithiation peak pair at 1.6–1.8 V vs. Li/Li⁺ (Figure 3B). This electrochemical signature is typical for orthorhombic Nb₂O₅.^{9,14} Similar to what we have observed in the m-Nb₂O₅/CDC, o-Nb₂O₅/CDC also showed a broad peak. The broadening becomes stronger as the cycle number increased.

To better understand the impact of the different degree defected structures of monoclinic and tetragonal phases of Nb₂O₅ on the electrochemical performance, we further

compared commercially available Nb₂O₅ (com-Nb₂O₅) and m-Nb₂O₅/CDC. As seen in Figure 3C, com-Nb₂O₅ depicts a much sharper lithiation and delithiation peak than that of m-Nb₂O₅/CDC, suggesting that lithium ions are hosted in the specific site in the structure of com-Nb₂O₅, whereas lithium ions are randomly diffused through the vacancies caused by stacking fault in the structure. The com-Nb₂O₅ also consists of vacancies caused by the stacking fault in the structure; however, m-Nb₂O₅/CDC reveals a higher degree of stacking fault (Figure 2A,D). Thus, the broadening redox peaks in m-Nb₂O₅/CDC are most likely caused by random diffusion of lithium in the structure.

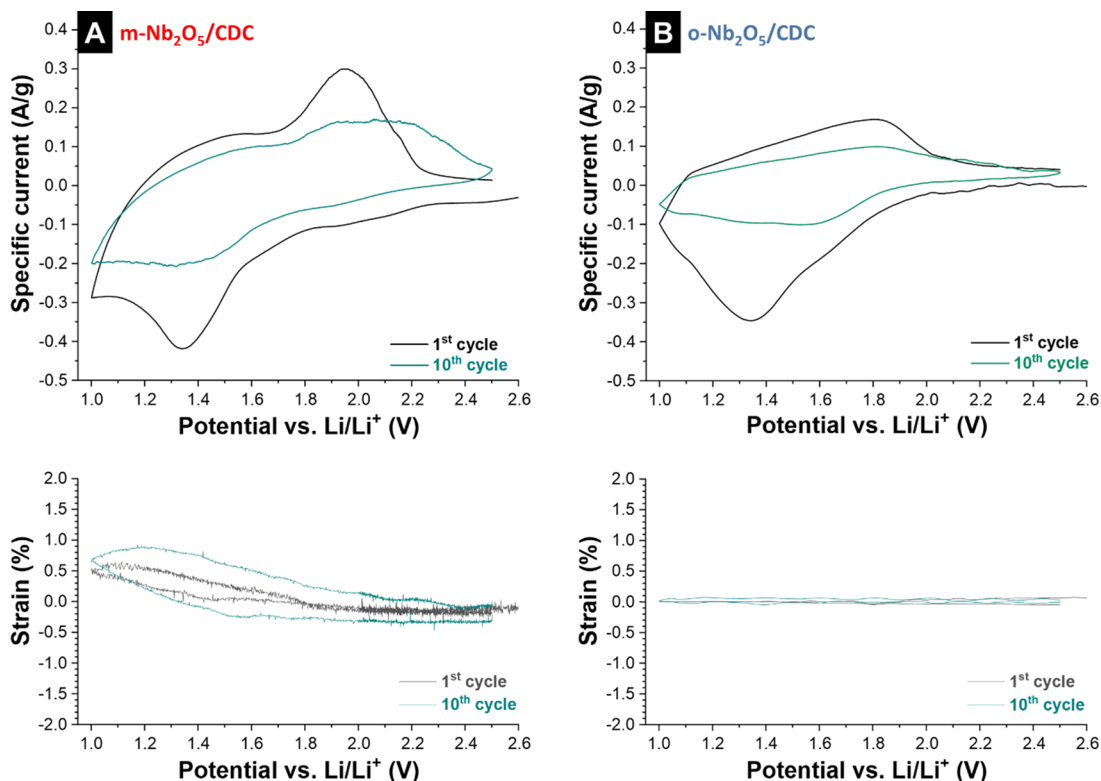


Figure 4. Electrochemical expansion curve (bottom) and the corresponding cyclic voltammogram (top) at 0.5 mV/s sweep rate of (A) m-Nb₂O₅/CDC and (B) o-Nb₂O₅/CDC recorded for the 1st and 10th cycle.

The galvanostatic charge/discharge operation at 0.01 A/g shows the ability of m-Nb₂O₅/CDC and o-Nb₂O₅/CDC to yield a charge storage capacity of about 300 mAh/g (Figure 3D). The profile shape aligns with the presence of several (m-Nb₂O₅/CDC and com-Nb₂O₅) or just one diffuse (o-Nb₂O₅/CDC) redox peak. The calculated capacity is normalized to the full mass of Nb₂O₅/CDC, that is, excluding the binder and carbon black but including the mass of CDC. This result is in contrast to the state-of-the-art in the Nb₂O₅ for use as a lithium-ion battery, where maximum insertion capacity was reported about 200 mAh/g (Supporting Information, Table S4).^{9,14} An excess of 200 mAh/g must also relate to a charge transfer process that involves three instead of two electrons in the voltage window (≥ 1 V vs. Li/Li⁺) of Li insertion to Nb₂O₅. For example, nanostructured monoclinic N₂O₅ also shows 242 mAh/g at a specific current of 0.05 A/g in the voltage window of 1.0–2.6 vs. Li/Li⁺, while box-implanted orthorhombic Nb₂O₅ nanorods provide a capacity of 247 mAh/g at 0.04 A/g in the voltage window of 1.1 to 3.0 V vs. Li/Li⁺ (Supporting Information, Table S4). The low amount of CDC and the limited charge storage via ion electrosorption of a material with <100 m²/g rule out the active role of carbon. Instead, the enhanced energy storage ability must relate to the intrinsic features of m-Nb₂O₅ and o-Nb₂O₅ instead, which are aided by the carbide-derive oxide-formation route and the presence of residual carbon. Oxygen deficiencies, as confirmed by the TGA results of m-Nb₂O₅/CDC and o-Nb₂O₅/CDC, are known to provide an increased specific capacity of lithium-insertion materials.^{62,63}

Table S4 in the Supporting Information shows that the high performance of Nb₂O₅ has been limited to nanoscaled materials, such as nanobelts, nanorods, or nanosheets.^{26,27} In contrast, our results demonstrate that it is possible for micrometer-scaled (bulk) materials to achieve high performance by careful design

of crystal structure defects as well. This approach is possibly adaptable to other bulk materials and may open new design concepts for advanced electrode material development.

Considering the interstitial sites for lithium accommodation, m-Nb₂O₅/CDC provides rather constrained space as compared with o-Nb₂O₅/CDC, which results in a higher barrier energy. However, the ion transport path within the structure of m-Nb₂O₅/CDC seems to be faster than that of o-Nb₂O₅/CDC. However, the charge transfer kinetics may also play a role because m-Nb₂O₅/CDC has a higher degree of graphitic carbon than that of carbon in the m-Nb₂O₅/CDC (Table 2). Based on the structures shown in Figure 2B,C,F, m-Nb₂O₅ may provide fast lithium diffusion due to its shorter mean free path per structure and small grain boundary. The material o-Nb₂O₅/CDC shows a zig-zag diffusion path resulting in higher kinetic energy. With the added effect of the large grain boundary, the electrochemical performance of o-Nb₂O₅/CDC is either limited by diffusion or charge transfer kinetics.

To this end, we conducted kinetic analysis by plotting the current at a specific potential versus the scan rate (Supplementary Information, Figure S6). Within such a current-vs.-scan rate plot, a slope of 0.5 (b value) corresponds to a diffusion-limited process, while a slope of 1.0 would be found for an ideal ion electrosorption process.^{64–68} When fitting data obtained for rates between 0.05 and 3 mV/s, we obtain for m-Nb₂O₅/CDC peak currents at 1.6 and 1.7 V vs. Li/Li⁺ and broad peaks for o-Nb₂O₅/CDC a b-value of ca. 0.5. This value is slightly smaller (i.e., more diffusion limited) compared to the com-Nb₂O₅ material with b values of 0.59–0.65. We further analyzed the cyclic voltammograms by using the method described by Ardizzone et al. (Supplementary Information, Figure S7).⁶⁷ The total charge scales well with the inverse of the square root of the

scan rate, which indicates the solid-state diffusion-limited process.

From Figure 3E, we see that m-Nb₂O₅/CDC is capable of performing faster charge/discharge as compared to the sample o-Nb₂O₅/CDC. From the kinetic analysis of the cyclic voltammograms (Supplementary Information, Figures S6 and S7), both materials are under diffusion control; thus, the superior rate handling of m-Nb₂O₅/CDC can be explained as follows: (1) o-Nb₂O₅/CDC possess a lower degree of graphitic carbon than that of m-Nb₂O₅/CDC, (2) o-Nb₂O₅/CDC has lower oxygen deficiency than m-Nb₂O₅/CDC, which causes lower conductivity, resulting in poorer rate handling performance,⁶⁹ (3) the particle size of m-Nb₂O₅/CDC (Figure 1C) is smaller than that of o-Nb₂O₅/CDC (Figure 1E), (4) the specific surface area of the o-Nb₂O₅/CDC (57 m²/g) is larger than that of m-Nb₂O₅/CDC (19 m²/g), while the microporous contribution as seen from the isotherm of o-Nb₂O₅/CDC is higher than that of m-Nb₂O₅/CDC (Supporting Information, Figure S3); thus, the combination of surface area and mesoporosity enables the electrolyte penetration throughout the material, resulting in higher capacity and better rate handling, (5) CDC distribution in the o-Nb₂O₅/CDC is poorer than that of m-Nb₂O₅/CDC (Supporting Information, Figure S8). At 10 A/g charge/discharge rate, m-Nb₂O₅/CDC possesses a specific capacity of 100 mAh/g, while o-Nb₂O₅/CDC completely loses the charge storage ability (Figure 3E). After 40 cycles of rate handling, both Nb₂O₅ largely recover their specific capacity at 0.01 A/g (288 mAh/g for m-Nb₂O₅/CDC and 274 mAh/g for o-Nb₂O₅/CDC). This different capacity between our m-Nb₂O₅/CDC and com-Nb₂O₅ might be explained by three main reasons: (1) the lower degree of defection in the structures of com-Nb₂O₅ compared to m-Nb₂O₅/CDC, (2) the significant larger particle size of com-Nb₂O₅ (Figure 1G) compared to m-Nb₂O₅/CDC (Figure 1C), and (3) the absence of the nanoscopic blending of Nb₂O₅ with carbon.

Performance stability was tested at a specific current of 0.1 A/g (Figure 3F). After 500 galvanostatic charge/discharge cycles, m-Nb₂O₅/CDC has maintained 72% of the specific capacity, while o-Nb₂O₅/CDC and com-Nb₂O₅ can maintain 66 and 55%, respectively. This obtained lower cyclic stability of com-Nb₂O₅ compared to m-Nb₂O₅/CDC and o-Nb₂O₅/CDC might be explained by the Coulombic efficiency ranges during the entire charge/discharge operation at values above 98% for all samples.

The performance stability of m-Nb₂O₅/CDC and o-Nb₂O₅/CDC is also aided by being virtually zero-strain materials during lithiation and delithiation. This absence of microstrain translates also to a zero-macrostrain as revealed by electrochemical dilatometry (Figure 4). The m-Nb₂O₅/CDC and o-Nb₂O₅/CDC materials display no significant compaction/expansion during Li⁺ insertion at the range of 1.3 and 1.9 V vs. Li/Li⁺. A slightly larger initial amplitude of strain is seen for m-Nb₂O₅/CDC of up to 1%, which increases for continued cycling (Figure 4A). The height change of o-Nb₂O₅/CDC remains stable at an amplitude below ±2% (Figure 4B).

Based on the half-cell data from galvanostatic charge–discharge, it is possible to construct a Ragone plot. While it is not suitable to compare the half-cell Ragone plot data with device-normalized performance, it still allows us to obtain a robust relative comparison between the three types of materials tested in our work. As seen in Figure 5, the performance of half-cells of m-Nb₂O₅/CDC and o-Nb₂O₅/CDC is very comparable,

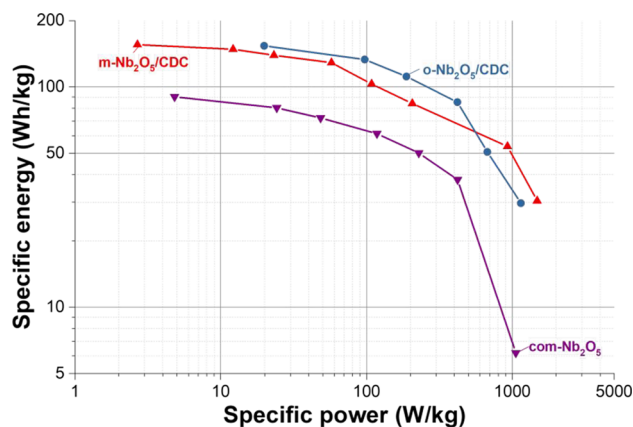


Figure 5. Ragone plot for half-cells of m-Nb₂O₅/CDC, o-Nb₂O₅/CDC, and com-Nb₂O₅.

while both samples are superior compared with com-Nb₂O₅. For example, the m-Nb₂O₅/CDC exhibits specific energies of 156 and 31 Wh/kg at specific power values of 3 W/kg and 1 kW/kg, respectively. In comparison, com-Nb₂O₅ delivers 90 Wh/kg at 5 W/kg and 6 Wh/kg at 1 kW/kg.

4. CONCLUSIONS

Niobium carbide is an attractive precursor for the synthesis of niobium pentoxide with enhanced electrochemical performance for use as a LIB anode material. Either by a two-step process of chlorination followed by oxidation in CO₂ or via one-step chloroxidation, we obtained Nb₂O₅/CDC hybrid materials with about 4 mass % of carbon. Carbide-derived o-Nb₂O₅/CDC and m-Nb₂O₅/CDC materials show a maximum capacity of about 300 mAh/g, which significantly exceeds the current state-of-the-art performance for Nb₂O₅ of about 200 mAh/g. Based on our results, we believe that the oxygen deficiency and the stacking faults in the Nb₂O₅ structures result in a superior capacity performance of Nb₂O₅/CDC as an anode for LIBs. Kinetically, o-Nb₂O₅/CDC exhibits slower charge/discharge performance compared to m-Nb₂O₅/CDC; the latter affords even 100 mAh/g at a high rate of 10 A/g. We also show evidence of robust cyclic stability over 500 cycles, suggesting a highly reversible lithiation/delithiation process, in alignment with a virtual zero strain material, as confirmed by electrochemical dilatometry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.9b02549>.

Results from the Rietveld refinement analysis, elemental composition analysis by XPS, scanning electron micrographs, transmission electron micrographs, Raman spectra and peak fitting analysis, nitrogen gas sorption isotherms, and electrochemical results (PDF).

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Notes

The authors declare no competing financial interest.

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