Graphical abstract

Synthesis and electrochemical properties of niobium pentoxide deposited on layered carbide-derived carbon

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Abstract

Herein we report on the hydrothermal synthesis of niobium pentoxide on carbide-derived carbon (Nb₂O₅/CDC) with a layered structure. The presence of phenylphosphonic acid guides the deposition during preparation, leading to the formation of amorphous Nb₂O₅ particles which are 4-10 nm in diameter and homogeneously distributed on the CDC framework. Electrochemical testing of the Nb₂O₅/CDC electrode indicated that the highest capacitance and Coulombic efficiency occurred using an electrolyte comprised of 1 M lithium perchlorate in ethylene carbonate/dimethyl carbonate. Subsequent heat treatment of Nb₂O₅/CDC in CO₂ environment led to crystallization of the Nb₂O₅, allowing reversible Li⁺ intercalation/de-intercalation. For sweep rates corresponding to charging and discharging in under 3 minutes, a volumetric charge of 180 C cm⁻³ and Coulombic efficiency of 99.2 % were attained.

Keywords: pseudocapacitor; niobium pentoxide; crystallization; nanocrystalline; hydrothermal

1. Introduction

Electrochemical capacitors (ECs), also called supercapacitors, are energy storage devices that can be rapidly charged/discharged and repeatedly cycled without significant capacitance decay [1]. ECs have been successfully commercialized and implemented in consumer electronics, transportation, back-up power systems, etc. [2,3]. Based on distinct charge storage mechanisms, ECs can be categorized into two primary types. Traditional

electrical double layer capacitors (EDLCs), which store charge by electrostatic adsorption of electrolyte ions on the electrode-electrolyte interface, typically rely on porous carbon electrodes with high specific surface areas [4]. The other type of ECs, pseudocapacitors, employ fast and reversible surface or near-surface redox reactions of electroactive species for charge storage [5].

Carbon materials are commonly used in EDLCs due to their low cost, high mechanical stability, good electrical conductivity, and high surface area [6,7]. While the ideal attainable capacitances reach 250 F g^{-1} for carbon materials with specific surface areas (SSA) of $>2000 \text{ m}^2 \text{ g}^{-1}$, the practical values are usually around 150 F g^{-1} due to the complexity of the pore structure, which limits the accessibility of electrolyte ions and restricts the surface area utilization [5]. One of the most promising approaches to greatly improve the limited specific capacitance (C_s) of carbon materials is by addition of redox-active (pseudocapacitive) species. For instance, nitrogen doping [8], and the deposition of transition metal oxides (TMOs) [9,10] or conducting polymers [11] onto the carbon framework has been shown to increase energy storage density significantly in various electrolytes.

Niobium pentoxide (Nb_2O_5) is considered to be one of the most promising transition metal oxides (TMO) for pseudocapacitive energy storage. It has been widely studied in lithium-ion batteries (LiB) [12], electrochemical hydrogenation catalysts [13], gas sensing [14], electrochromic devices [15] and solar cells [16]. Since its lithium intercalation potential closely matches the lowest unoccupied molecular orbitals (LUMO) of the organic

liquid-carbonate electrolyte [17], Nb_2O_5 is a safe anode with a high theoretical capacity of 200 mAh g^{-1} for LIBs. Nb_2O_5 exhibits a variety of crystalline allotropes, with orthorhombic ($T\text{-Nb}_2\text{O}_5$), pseudo-hexagonal ($TT\text{-Nb}_2\text{O}_5$), tetragonal ($M\text{-Nb}_2\text{O}_5$) and monoclinic ($H\text{-Nb}_2\text{O}_5$) [18,19] structures being the most common ones. The $T\text{-Nb}_2\text{O}_5$ phase is reported to be one of the most attractive pseudocapacitive materials due to its surface reaction and Li^+ intercalation. Dunn et al. showed fast lithium intercalation kinetics for $T\text{-Nb}_2\text{O}_5$, which was accompanied by little or no structural change [20]. The high intercalation pseudocapacitance of $T\text{-Nb}_2\text{O}_5$ could have several sources [21–23]. For example, Simon et al. found that the large pseudocapacitance is a consequence of the fast Li^+ intercalation capability within the (001) planes of the $T\text{-Nb}_2\text{O}_5$ [21], while Ganesh et al. concluded that the origin of high-rate intercalation pseudocapacitance is due to the unique open channels of NbO_x sheets that reduce the energy barrier and facilitate the local charge transfer between lithium and oxygen-containing structures [23].

Although Nb_2O_5 displays high levels of pseudocapacitance, its low electronic conductivity ($\sim 10^{-6} \text{ S cm}^{-1}$) [12] limits its performance. Moreover, it is important to note that all previously reported studies with this material relied on electrode thicknesses below 40 μm [21]. Undoubtedly, if the thickness is increased, volumetric capacitance would increase while power density would suffer. Therefore, increasing the conductivity and thickness of the electrodes while retaining their excellent energy density and power handling properties is critical. Previous efforts to address this problem include deposition of a carbon layer on the Nb_2O_5 nanocrystals to fabricate $\text{Nb}_2\text{O}_5\text{-C}$ core-shell composites

[24] and mixing of pseudo-hexagonal Nb₂O₅ powders with carbon nanotubes (CNTs) to form a Nb₂O₅/CNT composite [25]. In the latter case, the incorporated CNTs not only increased the conductivity of the electrode, but also provided additional capacitive storage [25]. However, only a few reports are available regarding the growth of Nb₂O₅ on carbon [26,27], and we are unaware of any results in which a highly crystallized *T*-Nb₂O₅ deposited on a carbon matrix was considered for pseudocapacitor application.

The work presented here represents the first report in which Nb₂O₅ nanoparticles were hydrothermally deposited onto a conductive carbide-derived carbon (Nb₂O₅/CDC) with a layered structure. The effects of phenylphosphonic acid addition during synthesis and the influence of electrolyte composition on the resulting electrochemical performance were studied systematically. A CO₂ oxidation treatment was developed which enabled us to obtain the desired *T*-Nb₂O₅ phase for improved capacitance. This study describes a new route for the synthesis of Nb₂O₅/carbon composites for pseudocapacitor electrodes in energy storage devices.

2. Materials and Experimental

2.1 Preparation of CDC

Titanium aluminum carbide (Ti₂AlC) powder was chosen as the carbon precursor because it produces mesoporous CDC with a graphene-like layered structure. Details of the chlorination procedure were described previously [28]. The Ti₂AlC powder (Kanthal, Sweden) was placed in the middle of a horizontal quartz tube, followed by Ar purge for 1 h at room temperature. Under continuous Ar flow, the temperature was raised to 800 °C

at a rate of $30\text{ }^{\circ}\text{C min}^{-1}$ and held for 1 h. The gas was then switched to Cl_2 , leading to complete etching by heating for 3 h at $800\text{ }^{\circ}\text{C}$ at a flow rate of 10 sccm, followed by H_2 treatment at $600\text{ }^{\circ}\text{C}$ for 2 h. The furnace was cooled to room temperature under Ar flow. The resulting carbide-derived carbon is subsequently referred to as CDC.

2.2 Preparation of $\text{Nb}_2\text{O}_5/\text{CDC}$

100 mg of CDC were sonicated in a 20 mL aqueous solution of 0.30 M ammonium niobate oxalate hydrate $\text{C}_4\text{H}_4\text{NNbO}_9 \cdot x\text{H}_2\text{O}$ (99.99 %, Sigma-Aldrich) and 0.33 M phenylphosphonic acid $\text{C}_6\text{H}_7\text{PO}_3$ (PPA, 98 %, Sigma-Aldrich) for 30 minutes. 400 mg of urea ($\text{CO}(\text{NH}_2)_2$, Sigma Aldrich) powder was added, and the mixed solution was subsequently transferred to a 40 mL Parr bomb for hydrothermal treatment at $200\text{ }^{\circ}\text{C}$ for 96 h. The product was rinsed with DI water and centrifuged several times until pH of the solution reached 7. Finally, the material, referred to as $\text{Nb}_2\text{O}_5/\text{CDC}$, was collected and dried at $100\text{ }^{\circ}\text{C}$ for 24 h. For comparison, $\text{Nb}_2\text{O}_5/\text{CDC}$ without PPA was also prepared.

2.3 Preparation of $\text{Nb}_2\text{O}_5/\text{CDC}-\text{CO}_2$

200 mg of $\text{Nb}_2\text{O}_5/\text{CDC}$ powders were loaded into a horizontal quartz tube furnace. After purging with Ar for 60 min, the furnace was heated under continuous Ar flow to $850\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and held for 30 minutes. The Ar gas was switched to CO_2 and kept for 1 h at $850\text{ }^{\circ}\text{C}$ at a flow rate of 10 sccm. The sample (referred to as $\text{Nb}_2\text{O}_5/\text{CDC}-\text{CO}_2$) was then cooled to room temperature in Ar. For comparison, CDC was treated using a similar method and is denoted as $\text{CDC}-\text{CO}_2$.

2.4 Materials characterization

The morphology of the materials was studied using scanning electron microscopy (SEM, Zeiss Supra 50VP, Germany) and transmission electron microscopy (TEM, JEM 2100, Japan). Specific surface area (SSA) and pore size distributions were evaluated by nitrogen sorption measurements at 77 K using a Quadrasorb gas sorption instrument (Quantachrome, USA). Samples were degassed at 120 °C for 24 h prior to the measurement. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method at the relative pressure (P/P_0) range of 0.05-0.2. The total pore volume (V_t) was calculated at $P/P_0=0.99$ while the pore size distribution was derived from quench-solid density functional theory (QSDFT) with an assumed slit-shaped pore geometry. The phases of the materials were studied via X-ray diffraction (XRD, Siemens D500, Germany). The carbon content of the Nb₂O₅/CDC material was determined using thermogravimetric analysis (TGA, TA Instruments, USA) *via* oxidation in air environment. During the measurement, samples were initially held at 100 °C for 1 h to remove any trapped water and subsequently heated to 800 °C at 2.5 °C min⁻¹.

2.5 Electrochemical characterization

2.5.1 Nanocrystalline electrode preparation

For initial electrochemical characterization, a nanocrystalline electrode, similar to what we have reported previously [18,20], was used. This approach maximizes the contact of every particle of the active material to the current collector, with ample electrolyte available to provide ionic conduction. No additional carbon or binder is needed as these electrodes were developed with the intent of directly characterizing the

active material of interest. Furthermore, only a small amount of active material is required. To make each electrode, 1 mg of active material is combined with 1 mL of ethanol and sonicated to form a dilute suspension of particles. 10 μL of this suspension is drop cast onto a 1 cm^2 section of stainless steel which has been cleaned by an O_2 plasma etch immediately prior to drop casting. The region outside the 1 cm^2 deposition area is masked with Mylar tape to avoid its contribution to the capacitive energy storage measurement. Each electrode is dried overnight at 120 $^\circ\text{C}$ under vacuum before being transferred into an Ar-filled glove box. The electrochemical properties of these nanocrystalline electrodes were characterized in a three-neck flooded cell using lithium foil as counter and reference electrodes.

2.5.2 Composite electrode preparation

A second type of electrode, which we term a composite electrode, was also prepared. This electrode is based on combining the electrochemically active material (the $\text{Nb}_2\text{O}_5/\text{CDC}$) with a carbon conductive agent (carbon black, 99.9%, Alfa Aesar) and a binder (polytetrafluoroethylene, or PTFE, 60 wt.%, Sigma–Aldrich). The materials were mixed in a mass ratio of 8:1:1 in ethanol (99.9 %, Fisherbrand). After evaporation of ethanol, the paste was rolled into a flat film, formed into electrode and vacuum dried for 24 h. Each working electrode was 1.5 mg in weight, 5 mm in diameter and 70 μm in thickness. Electrodes were also fabricated from YP-50F activated carbon (Kuraray, Japan, SSA of 1470 $\text{m}^2 \text{g}^{-1}$ and 0.85 nm pore diameter). These electrodes were prepared without adding carbon black. The mass ratio of YP-50F to PTFE was 95:5. Each YP-50F

electrode was 15 mg.

2.5.3 Electrolyte studies

Four types of electrolytes were prepared: 1 M lithium perchlorate in ethylene carbonate/dimethyl carbonate (1 M LiClO₄/EC/DMC), 1 M LiClO₄ in acetonitrile (1 M LiClO₄/AN), 1 M lithium hexafluorophosphate in ethylene carbonate/diethyl carbonate (1 M LiPF₆/EC/DEC) and 1 M lithium perchlorate + 1 M tetraethyl ammonium tetrafluoroborate (TEABF₄) in ethylene carbonate/diethyl carbonate (LiClO₄: TEABF₄ EC/DMC). The mixed solvents, EC/DMC and EC/DEC, used a 1:1 volume ratio.

2.5.4 Electrochemical characterization of composite electrodes

The electrochemical measurements of the Nb₂O₅/CDC composite electrodes were carried out using a three-electrode configuration in Swagelok cells. The Nb₂O₅/CDC composite served as the working electrode, an overcapacitive YP-50F electrode was the counter and Ag/AgCl was the reference electrode. Cyclic voltammetry (CV) at various sweep rates and galvanostatic charge-discharge (GCD) at different current densities were performed using a VMP3 potentiostat (Bio-Logic Inc., France). All the cells were cycled initially for 20 times at 20 mV s⁻¹. The stored charge was derived from the 20th cycle of cathodic CV using the following equation:

$$C_s = \int_{v_1}^{v_2} IdV/mv \quad (1)$$

while the Coulombic efficiency was derived based on the following equation:

$$\eta = \frac{C_{cathodic}}{C_{anodic}} \quad (2)$$

$$C_v = C_s \times \rho \quad (3)$$

Where, C_s ($C\ g^{-1}$) and C_v ($C\ cm^{-3}$) are, respectively, the gravimetric charge and volumetric charge of working electrode. I is the current response (mA), v_1 and v_2 represent, respectively, the initial and final potentials (V), v is the scan rate ($mV\ s^{-1}$), and m is the active mass (g) in one electrode. In Eqn. (2), η is the coulombic efficiency, $C_{cathodic}$ is the cathodic charge while C_{anodic} is the anodic charge. ρ ($g\ cm^{-3}$) is the bulk density of the electrode. All the reported electrochemical results were averaged from three parallel experiments.

3. Results and discussion

3.1 Materials synthesis

Figure 1 shows a schematic for the preparation of Nb_2O_5/CDC materials. The layered CDC synthesized at $800\ ^\circ C$ was chosen due to the presence of mesopores in the material and an adequate specific surface area ($\sim 800\ m^2\ g^{-1}$) [28], which is suitable for Nb_2O_5 deposition. After Nb_2O_5 was deposited hydrothermally onto/between the layers of the CDC, the material's microstructure resembled large bricks with severe aggregation (**Figure 1**, top circle). This can be explained by the i) hydrophobicity of the CDC surface and ii) high surface energy of Nb_2O_5 leading to the growth of larger agglomerates. In contrast, addition of the PPA into the synthesis suspension led to the homogeneous distribution of Nb_2O_5 particles on the CDC surface with a much smaller particle size, suggesting that PPA guides the uniform deposition of Nb_2O_5 nanoparticles. The likely explanation for this effect is that PPA modified the surface chemistry of CDC and, at least partially, terminated carbon with phosphonic acidic groups thus providing numerous

nucleation sites (see lower illustrations of **Figure 1**). As a result of the different composite morphologies, the electrochemical behavior of these composites is different, as discussed later.

3.2 Composite morphology and structure

The SEM image in **Figure 2a** and TEM image in **Figure 2c** indicates CDC has a layered morphology, which is derived from the layered Ti_2AlC precursor through a one-step chlorination process. After the hydrothermal treatment, the CDC surface becomes rougher (**Figure 2b**) and is decorated with uniformly distributed Nb_2O_5 particles (**Figure 2d**). The high resolution TEM image in **Figure 2e** shows that the Nb_2O_5 nanoparticles have sizes ranging from 4 nm to 10 nm. **Figure 3** shows SEM images of $\text{Nb}_2\text{O}_5/\text{CDC}$ after CO_2 oxidation. The layered structure of the composite material was maintained after heat treatment under CO_2 (**Figure 3a**), demonstrating that the mild oxidation process does not affect the overall structure of the $\text{Nb}_2\text{O}_5/\text{CDC}$. However, as revealed by higher magnification SEM images (**Figure 3b**), the Nb_2O_5 nanoparticles become more visible on the CDC layers, suggesting possible aggregation and growth of the oxide particles and also partial oxidation and removal of CDC substrate.

XRD was used to analyze the structure of the CDC and the as-prepared composite as shown in **Figure 4**. The broad [002] peak centered at $2\theta = 25^\circ$ signifies that CDC is amorphous to X-rays. After hydrothermally depositing Nb_2O_5 , the XRD pattern of the composite looks similar to CDC, suggesting that the 4 to 10 nm Nb_2O_5 nanoparticles are also X-ray amorphous. Because crystalline phases of Nb_2O_5 are beneficial for capacitive

energy storage [20,22], heating the Nb₂O₅/CDC composite is required for activating the the pseudocapitance.

Previous studies show that the *T*-Nb₂O₅ phase can be produced by heat treatment of amorphous Nb₂O₅ at temperatures higher than 600 °C in air or oxygen. However, oxygen-excessive environments are not suitable for the heat treatment of CDC/Nb₂O₅ hybrid materials as it results in the combustion of carbon. On the other hand, heat treatment in an oxygen-free environment (e.g., N₂ or Ar flow) will likely promote the formation of *TT*-Nb₂O₅. A comparison of structure of the *T*- and *TT*-Nb₂O₅ shows that the hexagonal unit cell of the latter phase contains only half of the formula equivalent (NbO_{2.5}), with one oxygen vacancy per unit cell [29]. Therefore, to achieve the desired *T*-Nb₂O₅ phase, it is preferable to carry out the heat treatment in an oxygen-containing environment. Accordingly, heat treatments were performed under CO₂ flow to provide a source of oxygen to reach the required ratio of Nb:O=2:5 and thus produce the desired crystalline phase. Being a milder oxidant in comparison to O₂ or air, CO₂ was not expected to lead to the complete oxidation of carbon. Our heat treatment studies confirmed this assumption.

As seen from XRD data (**Figure 4a**), CO₂ treatment of CDC had no significant effect on the graphitic structure of carbon, whereas sharp peaks centered at 22.6°, 28.4°, 36.5°, 42.8°, 44.2°, 46.1°, 50.1°, 55.2° and 58.5° appeared in the XRD pattern of Nb₂O₅/CDC samples after CO₂ annealing for 1 h at 850 °C. These peaks can be indexed as (001), (180), (181), (2100), (2110), (002), (380), (202), (2160) reflections of orthorhombic

(*T*-phase) Nb₂O₅, (JCPDS no. 30-0873) [22]. Moreover, peaks centered at 28.8°, 42.8° and 44.2° in Nb₂O₅/CDC-CO₂ clearly distinguish the *T*-phase Nb₂O₅ from other phases [22,30]. In addition to the peaks corresponding to *T*-Nb₂O₅, some lower intensity peaks were identified suggesting the presence of a small amount of the monoclinic Nb₂O₅ after the CO₂ treatment. For comparison, the XRD pattern of Nb₂O₅/CDC treated in Ar at the same temperature and duration is shown in **Figure 4b**. Close examination reveals that peaks centered at 22.6°, 28.5°, 36.7°, 46.2°, 50.6°, 55.3°, 59.1°, 64.9°, 70.8°, correspond to (001), (100), (101), (002), (110), (102), (200), (201), (112) reflections of pseudohexagonal Nb₂O₅ (*TT*-phase, JCPDS no. 28-0317), respectively. Thus, the treatment under CO₂ flow promotes the formation of the desired orthorhombic phase of Nb₂O₅.

The surface area and pore size distribution (PSD) of CDC and its composites were analyzed using N₂ sorption, as shown in **Figure 4c-d**. The type-IV isotherms suggest mesoporous structures for both materials. The PSD in **Figure 4d** reveals substantial volumes of micropores and mesopores in CDC, with a BET specific surface area (SSA) of 538 m² g⁻¹ and a pore volume of 0.506 cc g⁻¹, as shown in **Table 1**. Nb₂O₅ formation and pore blocking in CDC by Nb₂O₅ led to a decrease in SSA to less than 150 m² g⁻¹. The PSD of Nb₂O₅/CDC is similar to CDC (inset of **Figure 4d**) with the presence of mesopores, which are beneficial for electrolyte transport within the electrode. **Table 1** shows the porosity parameters of the CO₂ oxidized samples, revealing that CO₂ oxidation slightly increases the BET-SSA and pore volume in both samples. The combination of

results shown in **Figure 4** and **Table 1** indicates that CO₂ treatment has relatively little effect on morphology and graphitic content of CDC, but leads to crystallization of Nb₂O₅.

To determine the fraction of pseudocapacitive Nb₂O₅ in the composites, TGA was carried out in air (**Figure 5**). Both Nb₂O₅/CDC and Nb₂O₅/CDC-CO₂ have similar combustion onset temperatures (~400 °C) and temperatures of the maximum combustion rate (~550 °C, **Figure 5b**). The residual mass can be attributed to the remaining Nb₂O₅ in each composite, since the CDC exhibited a residue of < 1 wt.% (data not shown). The as-synthesized Nb₂O₅/CDC sample has a loading of 26 wt.% Nb₂O₅. This fraction increases to 45 wt.% because of partial oxidation of carbon during the annealing in CO₂. It should also be noted that the CO₂ thermal treatment could activate the CDC and lead to a higher electric double layer contribution to the total capacitance[31].

3.3 Electrochemical properties

3.3.1 The effect of PPA addition for nanocrystalline electrodes

As previously discussed, the addition of PPA into the hydrothermal synthesis guides the uniform deposition of Nb₂O₅, which is expected to exhibit improved electrochemical performance compared to the composite prepared without addition of PPA. We used nanocrystalline electrodes to quickly determine how the electrochemical properties changed for the different synthesis strategies. The nanocrystalline electrodes are useful for this application as each electrode only requires ~10 µg of active material, allowing for the fast and efficient screening of materials, similar to microelectrodes used in our previous studies [32]. As shown in **Figure 6**, Nb₂O₅/CDC-without PPA exhibits a CV

response with no evidence of Nb₂O₅ redox peaks. Moreover, the calculated specific capacitance is lower than CDC at all sweep rates, which could be attributed to the much lower SSA and poor utilization of the pseudocapacitive properties of Nb₂O₅ because of its aggregation. However, with the addition of PPA into the suspension, the composite shows a well-defined anodic peak at 1.5 V vs Li/Li⁺ and provides a much higher specific capacitance at all sweep rates, further verifying the PPA's positive effect on promoting utilization of Nb₂O₅. For convenience, all of the composites discussed in the following sections were prepared with the PPA addition. It should also be noted that for Nb₂O₅/CDC-with PPA (**Figure 6a**), the sharp peak on the cathodic sweep was due to lithiation of amorphous Nb₂O₅ and irreversible electrochemical reactions leading to electrolyte decomposition, as the Coulombic efficiency was only 95 %.

3.3.2 Electrolyte studies

The experiments directed at the effect of Li⁺ containing electrolyte systems were carried out on the Nb₂O₅/CDC composite electrodes (**Figure 7**). The broad cathodic peak observed in the anodic sweep in all electrolyte systems (**Figure 7a**) indicated the delithiation of amorphous Nb₂O₅. It was found that 1 M LiClO₄/EC/DMC provided a high Coulombic efficiency (96-99 %) even at relatively low scan rates (**Figure 7c**) without compromising specific capacitance values (**Figure 7b**). This electrolyte system was therefore selected for use in the more detailed electrochemical studies.

3.3.3 Effect of Nb₂O₅ phase content

The results shown in **Figure 8** summarize how the capacitive storage properties of the

composite electrodes are influenced by the presence of Nb₂O₅ and the CO₂ treatment. For the CDC, a typical rectangular CV shape is observed throughout the entire potential range (-1.8 to 0 V vs Ag/AgCl) indicating pure capacitive behavior during the charge/discharge process arising from electric double-layer capacitance. At 10 mV s⁻¹, CDC provided ~ 100 C g⁻¹. This value is less than the result (140 C g⁻¹) for nanocrystalline electrodes of CDC (Figure 6), however, the loading for the CDC electrodes in Figure 8, 7.6 mg cm⁻², is more than 50 times greater than that of the nanocrystalline CDC electrodes. The capacitance of the CDC at sweep rates greater than 10 mV s⁻¹ is relatively unaffected by the CO₂ heat treatment (Figure 8b). This result shows that CO₂ oxidation of CDC under the same conditions as Nb₂O₅/CDC-CO₂ did not have much effect on its electrochemical performance. The deposit of amorphous Nb₂O₅ onto CDC (i.e., Nb₂O₅/CDC) increased the specific capacitance over the entire range of sweep rates. Such an increase originates from the additional pseudocapacitive contribution of the Nb₂O₅, as seen from the broad redox peaks between -1.8 V and -0.8 V (vs Ag/AgCl).

As shown in Figure 4a, CO₂ treatment leads to crystallization of the amorphous Nb₂O₅ and the formation of orthorhombic and monoclinic phases. The oxidized Nb₂O₅ features two pairs of redox peaks at -1.55/-1.35 V and -1.32/-1.12 V (vs Ag/AgCl). Moreover, the composite sample is characterized by i) good rate handling capability (Figure 8b), ii) well-defined cathodic and anodic peaks at various scan rates (Figure 8c), iii) a higher Coulombic efficiency compared to amorphous Nb₂O₅ (Figure 8d) and iv) highly reversible lithiation/delithiation processes. As a result, Nb₂O₅/CDC-CO₂ shows the

highest stored charge - 220 C g⁻¹ at 1 mV s⁻¹, which decreases to 157 C g⁻¹ at 10 mV s⁻¹, as shown in **Figure 8b**. The relative amount of capacitance decay with increasing sweep rates is comparable to that of the CDC component, suggesting that the carbon architecture is not optimized. **Figure 9a** presents the GCD profiles of Nb₂O₅/CDC-CO₂. The deviation from the linear profile below -1.2 V is consistent with the mechanism regarding the additional charge storage contribution. Moreover, the small IR drop at 2 A g⁻¹ indicates the good power handling properties of the Nb₂O₅/CDC. The increase in capacitance can also be inferred from the GCD profile in **Figure 9b**, as prolonged charge-discharge time was found in Nb₂O₅/CDC-CO₂ at 1 A g⁻¹.

The present paper provides insight regarding the capacitive energy storage properties one can expect upon adding a pseudocapacitive component to a carbon-based support. As mentioned previously, the former stores charge by a redox reaction while the latter involved electrical double layer processes. Here again we characterize the charge storage in terms of C g⁻¹ to analyze the respective contributions. For Nb₂O₅, the theoretical value for forming Li₂Nb₂O₅ from Nb₂O₅ is 728 C g⁻¹. The effect of adding Nb₂O₅ to CDC for increased energy storage is shown in **Table 2**. Again, we have used the data taken at 10 mV s⁻¹ since 3 minutes of discharging and charging represents a reasonable time frame for energy storage based on capacitive processes for both electrical double layer and pseudocapacitance. The results show that by adding Nb₂O₅, the stored charge increases, demonstrating the pseudocapacitance contribution from the Nb₂O₅ redox sites. However, the energy storage properties for the Nb₂O₅/CDC and Nb₂O₅/CDC-CO₂ composites are

only 40%-50% of their computed values based on the compositions used in the study. We attribute this behavior to there being much less pseudocapacitance contributed from the Nb₂O₅ phase. In fact, if we assume that the CDC contributes the same relative amount of charge storage based on control experiments (see **Table 2**), then Nb₂O₅ provides only about 60 C g⁻¹ for amorphous Nb₂O₅ and 100 C g⁻¹ for crystalline Nb₂O₅. These values are far below what is expected for the pseudocapacitive contribution from Nb₂O₅. The reason for this less than expected pseudocapacitive response is likely to be a combination of factors including poor electrical contact between the carbon and Nb₂O₅ and occluding the Nb₂O₅ surfaces so that electrolyte is not accessible to the redox-active material. Electrolyte access may be the key here as a more porous composite that used carbon nanotubes with Nb₂O₅ (pseudohexagonal) exhibited greater gravimetric charge storage (~ 400 C g⁻¹) although with lower volumetric charge storage [23].

Another consideration with the Nb₂O₅/CDC composites is their power handling properties. It is not surprising that the high rate performance of the Nb₂O₅/CDC-CO₂ electrodes is less impressive than our earlier work with nanocrystalline electrodes [20] as the electrodes used in the current study were 70 µm thick and contained insulating PTFE binder. The density of the Nb₂O₅/CDC-CO₂ electrode, however, was 1.1 g cm⁻³, a significantly greater value. Thus, the highest volumetric charge reaches 242 C cm⁻³ at 1 mV s⁻¹. Moreover, the volumetric capacitance for the Nb₂O₅/CDC-CO₂ electrode exceeds 180 C cm⁻³ (100 F cm⁻³) at sweep rates corresponding to the 3 minutes charge and discharge conditions mentioned above. These values are higher than, for example,

three-dimensional MnO_2 /carbon nanofoams (90 F cm^{-3}) over the same charge-discharge time range [33]. It should also be noted that the Coulombic efficiency reached values as high as 99.2 % at 10 mV s^{-1} . Future efforts will focus on further optimization of conductivity of the Nb_2O_5 /CDC, while increasing the loading of $T\text{-Nb}_2\text{O}_5$, leading to higher gravimetric and volumetric capacitances in combination with good power handling.

4. Conclusions

Nb_2O_5 /CDC composites with a layered structure were prepared by the hydrothermal deposition of Nb_2O_5 on the surface of CDC. Amorphous Nb_2O_5 nanoparticles on the order of 4-10 nm were homogeneously distributed on the CDC surface when phenylphosphonic acid was added. High-temperature treatment in CO_2 was found to be effective in converting the amorphous Nb_2O_5 into orthorhombic and monoclinic phases without degrading the CDC support. This treatment resulted in improved electrochemical characteristics such as reversible Li^+ intercalation/de-intercalation, increased gravimetric capacitance (157 C g^{-1}), higher volumetric capacitance (180 C cm^{-3}) and Coulombic efficiency of 99.2 % at a charge-discharge time of 3 minutes. Thus, annealing in CO_2 offers a simple and environmentally benign method of obtaining crystalline niobium pentoxide with increased energy storage properties.

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Figure 2. Morphological studies of the CDC substrate and the Nb₂O₅/CDC composite: SEM images of (a) CDC and (b) Nb₂O₅/CDC composite; TEM images of (c) CDC, (d) Nb₂O₅/CDC composite and (e) Nb₂O₅/CDC composite at a higher magnification.

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Figure 5. Thermal analysis studies of Nb₂O₅/CDC composites with/without CO₂

heat-treatment: (a) use of TGA to determine the fraction of Nb₂O₅ in the composites; (b) use of DTA to determine the onset of carbon oxidation and oxidation rate.

Figure 6. Electrochemical studies using nanocrystalline electrodes of the Nb₂O₅/CDC composites in 1 M LiClO₄ in EC/DMC. The results show the effect of using PPA in hydrothermal synthesis of the composites: (a) voltammetry sweeps at 10 mV s⁻¹ and (b) sweep rate dependence of charge storage.

Figure 7. Electrochemical properties of Nb₂O₅/CDC composite electrodes in different electrolytes tested in a three-electrode Swagelok cell: (a) voltammetric sweeps at 5 mV s⁻¹; (b) sweep rate dependence of charge storage; (c) Coulombic efficiency as a function of sweep rate.

Figure 8. Electrochemical characterization of the CDC and Nb₂O₅/CDC composite electrodes: (a) voltammetry sweeps for the various materials at 2 mV s⁻¹, the well-defined peaks in Nb₂O₅/CDC-CO₂ indicate that the Nb₂O₅ nanoparticles have crystallized; (b) total charge storage (gravimetrically normalized) as a function of sweep rate; (c) voltammograms for the Nb₂O₅/CDC-CO₂ composite at different sweep rates, demonstrating the high power handling properties of the material; (d) Coulombic efficiency as a function of sweep rate for Nb₂O₅/CDC and Nb₂O₅/CDC-CO₂

Figure 9. Galvanostatic charge-discharge characteristics for CDC and composite electrodes: (a) Nb₂O₅/CDC-CO₂ at different current densities; (b) charge-discharge comparison of CDC, Nb₂O₅/CDC and Nb₂O₅/CDC-CO₂ at 1 A g⁻¹

Table 1. Porosity parameters of CDC and Nb₂O₅/CDC

Sample	BET-SSA (m ² g ⁻¹)	DFT-SSA (m ² g ⁻¹)	Pore volume (cc g ⁻¹)	Pore diameter (nm)
CDC	538	501	0.506	0.723
Nb ₂ O ₅ /CDC	116	106	0.123	0.666
CDC-CO ₂	591	551	0.694	0.671
Nb ₂ O ₅ /CDC-CO ₂	125	112	0.132	0.659

Table 2. Charge contribution for each component in the composites

Samples	Content (%)		Contributions to stored charge (C g ⁻¹) ^a		Stored charge (C g ⁻¹)	
	CDC	Nb ₂ O ₅	CDC	Nb ₂ O ₅	Expected ^b	Measured ^c
CDC	100	-	100	-	-	100
CDC-CO ₂	100	-	104	-	-	104
Nb ₂ O ₅ /CDC	74	26	74	189	263	131
Nb ₂ O ₅ /CDC-CO ₂	55	45	57	327	384	157

^a Values for CDC based on experimental result of 100 C g⁻¹ at 10 mV s⁻¹ for pure component; values for Nb₂O₅ component based on charge storage for fully lithiated Nb₂O₅ (728 C g⁻¹);

^b expected stored charge based on the equation: $C_{\text{expected}} = C_{\text{Nb}_2\text{O}_5} * w_{\text{Nb}_2\text{O}_5} + C_{\text{CDC}} * w_{\text{CDC}}$
where $C_{\text{Nb}_2\text{O}_5} = 728 \text{ C g}^{-1}$ and $C_{\text{CDC}} = 100 \text{ C g}^{-1}$ or 104 C g^{-1} for CO₂ treated;

^c stored charge measured at 10 mV s⁻¹.

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