Capacitance Response in an Aqueous Electrolyte of Nb₂O₅ Nanochannel Layers Anodically Grown in Pure Molten *o*-H₃PO₄

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Abstract

Vertically aligned Nb₂O₅ nanochannel layers are grown on Nb metal substrates by self-organizing electrochemical anodization in a pure molten *o*-H₃PO₄ electrolyte. The capacitive behavior of these structures, as negative electrodes (from -0.2 to -1.25 V vs. SCE), is investigated in aqueous 1 M Na₂SO₄ electrolyte. The surface chemistry, morphology and crystallographic features of the Nb₂O₅ nanochannel electrodes is tailored by adjusting the synthesis parameters, namely anodization time and crystallization temperature, which have a significant effect on the electrode performance. Nb₂O₅ nanochannel layers, 8 μm thick, and converted into orthorhombic phase by crystallization at 450°C, display a maximized areal capacitance of ~ 100 mF cm⁻² at a current density of 1 mA cm⁻². These electrodes retain 63% of the initial capacitance at 10 mA cm⁻² and 81% after 1500 charge-discharge cycles. Kinetic analysis of the electrochemical results reveals the occurrence of pseudocapacitive and diffusion-controlled processes. Electrochemical impedance spectroscopy (EIS) evidences for these structures low resistances across the electrode and at the electrode/substrate interface. This result is associated to the nanochannel morphology (high active area) of the Nb₂O₅ layers, and to their crystalline nature, which provide an “oriented porosity” for ion diffusion and directional pathways for charge collection.

Introduction

Energy sustainability and environmental concerns are pushing the scientific community to develop reliable environmentally-friendly renewable sources of energy. In the recent years, the development of alternative energy technologies, particularly based on solar, wind and wave technologies has been accelerated. However, cost-effective energy storing and its supply at a reasonable price is still a prime challenge, especially if compared to non-renewable sources (e.g. coal). In this context, battery and supercapacitor technologies have been developed for energy storage/supply; however, research efforts are still required towards higher device efficiencies and cost competitiveness.

Over the last years, batteries have been explored more thoroughly than supercapacitors. However, supercapacitors possess interesting properties, such as a faster charge-discharge rate, longer cycle life and ability to deliver up to ten times more power than batteries, that make them attractive for a wide range of applications [1]. Thanks to these properties supercapacitors, and particularly redox supercapacitors, can either complement or replace batteries in some applications. The basic reason for the superior properties of redox supercapacitors compared to conventional batteries is based on their charge storage mechanism.

Presently, rechargeable batteries, e.g. aqueous based Ni-MH batteries and non-aqueous Li-ion batteries, mainly store charge either by bulk diffusion or intercalation/deintercalation of cations (H^+ or Li^+). As a consequence, the electrode material typically undergoes changes to form different compositions/phases [2, 3]. This process is diffusion-controlled, which makes it sluggish and thereby restricts the maximum charge-discharge rate (or power density).

However, in the case of nearly pseudocapacitive materials, the cations electrochemically adsorb on the surface of the material through charge transfer processes or intercalate into the Van der Waals gaps in the case of e.g. a layered material. Both processes are associated with reduction

of metal atoms located either at the surface or in the interlayer lattice planes. However, the electrochemical adsorption of charge at the surface is kinetically favored; on the other hand, the intercalation process (kinetics) is relatively slow. Nevertheless, in some cases it has been noted that diffusion of cations into the Van der Waals gaps can be fairly facile and, therefore, it can be regarded as a capacitive phenomenon, generally termed as intercalation pseudocapacitance [4, 5]. Conway and co-workers defined this process as pseudocapacitive since cations are faradaically stored without any phase or compositional changes [4, 6]. In other words, the reactions should be kinetically (and not diffusion) controlled on the time scale of interest, thus occurring at higher rate compared to diffusion controlled processes.

Some transition metal oxides generally possess pseudocapacitive nature. For this reason, they are emerging as promising candidates for capacitive electrodes due to high energy storage ability, which can be almost one order of magnitude higher than electric-double layer capacitors (EDLCs) based on carbon electrodes.

To design more efficient and versatile supercapacitors, “asymmetric systems” have been developed, where materials active in negative and positive potentials versus the reference electrode are clubbed together to widen the working potential window. This also leads to improved energy density.

Different forms of carbon based materials are commonly used as negative electrode, and are investigated for most of the asymmetric set up using metal oxides as positive electrode. However, in carbon-based electrodes the capacitive response is solely based on the double layer and the electrode displays very low energy density, which restricts the overall performance.

Alternatively, metal oxides active as negative electrodes are comparably still less explored in spite of their potential. In this context, various metal oxide based materials that are active in the negative potential range, have been meanwhile explored, and showed outstanding capacitive

behavior in asymmetric setup. Examples are iron based materials (in forms of oxides [7, 8], oxyhydroxide [9], and composites with conductive components such as multi-walled nanotube [10], graphene [11, 12], polyaniline (PANI) [13]), MoO_x of different stoichiometries [14, 15] (including its composite with graphene [16], polypyrrole [17], VOS@C [18]), WO_3 [19, 20] and Bi_2O_3 [21].

Particularly, Nb_2O_5 , which has been investigated for various applications such as gas sensing, electrochromics, catalysis, and photoelectrochemistry among other, is an attractive candidate also for battery anodes and for supercapacitors. The reason is its ability to switch between different oxidation states such as +5 in Nb_2O_5 , +4 in NbO_2 , +3 in Nb_2O_3 and +2 in NbO [22-26]. The electrochemical behavior of Nb_2O_5 was first investigated by Bard et al., who noticed its cation insertion/deinsertion behavior (and consequent tunable color change) [27, 28]. Nb_2O_5 has been also extensively studied for Li-ion battery anodes (negative electrode) owing to its higher theoretical capacity ($\sim 200 \text{ mA h g}^{-1}$) compared to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (175 mA h g^{-1}) [29].

However, in general Nb_2O_5 suffers from poor electron conductivity ($\sigma \sim 3 \times 10^{-6} \text{ S cm}^{-1}$) that limits its use to only low voltage-lithium batteries rather than for supercapacitors [30]. Several efforts have been made to improve its electronic conductivity, e.g. by exploring different crystallization pathways and phases, morphologies, and use/elimination of additives (to enable fast and reversible charge storage). Brezesinski et al. found that iso-oriented crystalline domain of group V transition metal oxides, including Nb_2O_5 , show improved charge storage performance because such a crystalline nanostructure provides additional pseudocapacitive response by allowing fast and reversible cation diffusion into the layered structure compared to both amorphous or randomly-oriented crystalline structures [5, 31]. Moreover, Kim et al. outlined the effect of crystallinity and the role of various phases on the pseudocapacitive behavior of Nb_2O_5 oxides – they observed that particular crystalline phases such as the

orthorhombic and the pseudohexagonal show enhanced pseudocapacitive behavior. The reason, also in this case, is the insertion of Li^+ ions through defined and oriented pathways in the Nb_2O_5 structure [32].

Therefore, the electrode material morphology plays an important role in tuning the diffusion path length for ions and material capacitive behavior. Furthermore, nano-sized structure generally shortens the ions diffusion path length and increases the contact area between electrode material and electrolyte. Among different morphological variations, one dimensional (1D) nanostructures such as nanowires, nanofibers, nanotubes were proved to be efficient charge storage materials owing to directional electronic and ionic transport, contrasting to 0 dimensional (0D) materials such as nanoparticulate layers, where disconnected nanoparticles lowers the ionic transportation and electronic conductivity [33-35].

Another strategy to improve the electronic properties of Nb_2O_5 is to use it in combination with highly-conductive materials such as graphene [34, 36], and carbon nanotubes (CNTs) [37, 38]. To improve further the capacitive response of the material one relevant issue is to reduce or to eliminate additives/binders. This can be easily achieved by growing the electrode active material directly onto a metal substrate and also lowers the electrode/collector interface resistance [15, 39].

At authors' best knowledge this work reports, for the first time, the supercapacitive behavior of anodic Nb_2O_5 nanochannel layers in an aqueous electrolyte, in a negative potential window vs. SCE. The Nb_2O_5 electrodes were synthesized by anodizing Nb metal substrates into pure molten *o*- H_3PO_4 followed by annealing [40]. The anodization time and annealing temperature were investigated to maximize the capacity behavior. The best performance was achieved for anodized Nb_2O_5 nanochannel layers grown for 12 h and then annealed at 450°C. The maximum specific capacitance obtained was 100.1 mF cm^{-2} at 1 mA cm^{-2} , with a capacitance retention of

63 % at 10 mA cm^{-2} . Based on the promising results, it is expected that such Nb_2O_5 structures can be used as negative electrode material for asymmetric supercapacitor setups.

Experimental Section

Synthesis

Nb_2O_5 electrodes were grown as self-organized vertically-aligned nanochannels by electrochemical anodization of Nb metal substrates in pure molten ortho-phosphoric acid (*o*- H_3PO_4) [40]. Nb foils (0.125 mm, 99.9% purity, Advent Research Materials LTD, Oxford, UK) were cut into $1.0 \times 2.0 \text{ cm}^2$ pieces, cleaned by ultra-sonication in acetone, ethanol and de-ionized water (10 min each) and then dried in a N_2 stream. For the anodization experiment, a two-electrode electrochemical cell was used, where the Nb and Pt foils were the working and counter electrodes, respectively. The two electrodes were immersed into the molten hot electrolyte in a vertical configuration and were placed at a distance of 2 cm from each other. The nominal area of the Nb foil that was immersed into the hot electrolyte (anodic area that grows the porous oxide layer) was of $1.0 \times 1.0 \text{ cm}^2$ per each side of the Nb foil, thus giving a total nominal anodic area of $\sim 2 \text{ cm}^2$.

The electrolyte, i.e. (nominally) pure molten *o*- H_3PO_4 (99%, Emsure), was constantly stirred during the anodization experiments and kept at the desired temperature (100°C) by thermostatic control provided by a heating-stirring plate that was equipped with a Teflon-lined thermocouple immersed into the anodizing medium.

The experiments were performed under potentiostatic conditions applying a constant anodic bias of 5 V (no sweeping) provided by a Volcraft VLP 2403 Pro power supply. The resulting

current (density) was recorded by using a Keithley 2100 6 1/2 Digit multimeter. The duration of the anodization experiments varied from 0.5-24 h.

After anodization, the anodic oxide layers were rinsed with water and were dried with a N₂ stream. The as-formed anodic oxide layers (typically amorphous) were converted into crystalline (orthorhombic) Nb₂O₅ layers by annealing in a tubular furnace, in air, at different temperature in the 350-550°C range. Both the amorphous and the crystalline layers were explored as electrode for supercapacitors.

Physico-chemical characterization

A Hitachi field emission scanning electron microscope (FE-SEM S4800, Hitachi) was used for morphological characterization of the samples. The thickness of the nanostructured films (as well as that of the barrier layers and thermal oxide layers formed underneath) was assessed by SEM analysis of cross-sectional cuts of the anodic layers, which were prepared by Ar-ion milling. X-ray diffraction (XRD) patterns were collected using an X'pert Philips PMD diffractometer with a Panalytical X'celerator detector, using graphite-monochromized Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The chemical composition of the anodic layers was determined by X-ray photoelectron spectroscopy (XPS, PHI 5600, US). XPS spectra were acquired using monochromatic Al X-rays source with a pass energy of 23.5 eV. The XPS spectra were corrected in relation to the C1 s signal at 284.8 eV.

Electrochemical characterization

The anodized and annealed niobium oxides were used directly as working electrode. Capacitive behavior of all the samples were evaluated by performing cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements. CV was done in the potential window of

-0.2 to -1.3 V vs. SCE at varying scan rate ranging from 10 to 100 mV s⁻¹ and GCD was performed in the potential window of -0.2 to -1.25 V vs. SCE at different current densities ranging from 1 to 10 mA cm⁻². All the measurements were performed in freshly prepared 1 M Na₂SO₄. Platinum and saturated calomel electrode (SCE) were used as counter and reference electrode in the three electrode measurement setup and niobium oxide samples as working electrode. A Voltalab PGZ 100 potentiostat was used for the measurement of CV and GCD. The electrochemical behaviour was also evaluated by electrochemical impedance spectroscopy (EIS) using a Gamry interface 5000 E instrument. The experiments were performed at open circuit potential (OCP) in the frequency range from 0.01 Hz to 10⁵ Hz using 10 mV sinusoidal perturbation.

Results and Discussion

Fig. 1a shows the characteristic current density-time (*J*-*t*) profile of a Nb oxide nanochannel layer grown after a 5 h-long anodization. The temperature of the electrolyte (molten *o*-H₃PO₄) was 100°C and the applied voltage was 5 V. After a sudden current density increase up to ca. 5-10 mA cm⁻² upon applying the anodic bias, *J* rapidly decreases within 5 min and reaches a constant value, i.e. steady state *J* of ~ 0.5 mA cm⁻². Such a *J*-*t* behavior is similar to that of other anodically formed self-organized one-dimensional (1D) oxide nanostructures (a most common example is TiO₂ nanotube arrays) [41, 42]. In the first stage of the anodization (*J* increases) the Nb metal substrate forms a compact oxide film at the metal/electrolyte interface. Afterwards, localized etching of the compact anodic oxide begins at random sites, forming irregular pores that grow in depth. After a few minutes (Fig. 1a, Inset), an equilibrium is established (steady state conditions) between the metal oxide growth and the field-assisted electrochemical dissolution of the formed oxide, and the resulting anodic Nb oxide grows in the form of

vertically-aligned nanochannels. The openings (pores) of the nanochannels at the top of the anodic layer are homogeneous and ~ 7 nm-sized (Fig. 1b, c). These nanochannels are vertically aligned and remain open from the top to the bottom of the structure (Fig. 1b right). For an anodization time of 1 h, the nanochannel layer is ~ 800 -900 nm-thick.

Figure 1

(a) J - t characteristic of a Nb oxide nanochannel layer grown (anodization time = 5 h). Inset: J - t profile during the first 10 min of anodization. (b) Top (left) and cross-section (right) SEM images of a Nb oxide nanochannel layer formed by 1 h-long anodization. (c) Pore (nanochannel) size distribution of the anodic layer in (b).

Nevertheless, the length of the Nb oxide nanochannels (Fig. 2a) can be adjusted by controlling the anodization time. Fig. 2b shows that the layer growth rate is constant (in average ~ 830 nm h⁻¹) when the anodization experiments are as long as 5 h. For anodization times ~ 10 h the overall oxide growth rate slightly decreases – the reason is that the top of the oxide structure undergoes corrosion as it is exposed to the etching electrolyte for a long time. For anodization

times > 12 h (e.g. 24 h) the oxide layer is significantly thinner than after a 12 h-long anodization (i.e. 5 vs. 8 μm).

Figure 2

(a) Correlation between anodic Nb oxide thickness (nanochannel length) and anodization time.

(b) SEM images of (left) ion-milled cross-section and (right) top view of Nb nanochannels layers grown by 5, 12 and 24 h-long anodization experiments and annealed at 450°C (1 h, in air).

The reasons for this can be (i) a substantial etching of the top of the anodic structure, and (ii) a relatively slower oxide growth at the metal/oxide interface caused by the thick oxide and the electric field drop [42] – in other words, the oxide etching is faster than the oxide anodic growth. A typical morphological feature resulting from an “extended anodization” (≥ 12 h) is the formation at the top of the anodic layers of needle-like structures formed by a partial corrosion and collapse of the nanochannel sidewalls (Top view images and Inset in Fig. 2b – 12 and 24 h) [43].

As shown by the XRD patterns in Fig. 3a, the as-formed (af) anodic layers are amorphous, and only reflections of the Nb metal substrate can be detected [44]. However, crystallization of the nanochannel structures into orthorhombic Nb₂O₅ begins upon annealing at 350°C (in air, 1h) [45]. Higher annealing temperature (450 and 550°C) lead in general to a higher degree of crystallization for both layers grown by 5 and 24 h-long anodization experiments (Fig. 3a and Fig. 3b, respectively).

Figure 3

XRD patterns of Nb oxide nanochannel layers as-formed and annealed at different temperature. Anodization time of (a) 5 h and (b) 24 h.

The chemical composition of the structures was analyzed by XPS – data are compiled in Fig. 4. The XPS survey (Fig. 4a) shows that the anodic layers are mainly composed of Nb and O, with small amounts of P (from the anodizing electrolyte) and adventitious C. High resolution XPS spectra in the Nb3d, O1s and P2p are shown in Fig. 4b-d. In any case, a 0.5 eV shift of the B.E. towards higher values was observed upon annealing (and consequent crystallization) at

450°C. This result is probably due to desorption of e.g. C species (see Table 1) from the Nb₂O₅ nanochannel surface during the annealing in air at 450°C.

The Nb3d doublet (Nb3d_{3/2} and Nb3d_{5/2}) of sample 5h-450°C (Fig. 4b) shows peaks at 210.5 and 207.9 eV, which is in line with Nb⁵⁺ state in Nb₂O₅ [46, 47]. The O1s signal (Fig. 4c) for annealed structures is at 531.1 eV, which is consistent with O bound in crystalline Nb₂O₅ [46]. In contrast to that of annealed structures, the O1s signal for as-formed nanochannels shows a shoulder at 533.0 eV. The peak at lower B.E. (531.1 eV) is originated from lattice oxygen, while the shoulder at higher B.E. (533.0 eV) is ascribed to adsorbed water molecules (H₂O_{ads}) and surface hydroxyl terminations (-OH) [48] that are desorbed with annealing.

Figure 4

XPS data of as-formed and annealed (450°C, 1 h, in air) Nb₂O₅ nanochannel layers grown by 5 h-long anodization experiments: (a) survey; (b-d) high resolution photoelectron spectra measured in the (b) Nb3d, (c) O1s and (d) P2p regions.

Table 1 summarizes the chemical composition of amorphous and crystalline layers determined from XPS data. One can notice that P is present at the surface of the Nb₂O₅ structures even after annealing (evident also in Fig. 4d), contrasting to what observed for C, which is burned off (forming CO₂) upon heat treatment in air.

Table 1

Sample	Surface content (at%)				Nb:O ratio*
	Nb	O	P	C	
5h-af	18.3	63.2	5.90	12.6	0.29
5h-450°C	22.4	67.0	6.20	4.40	0.33

* Nb:O ratio in stoichiometric Nb₂O₅ = 0.40

Nb, O, P and C composition determined by XPS analysis of as-formed and annealed (450°C, 1 h, in air) Nb₂O₅ nanochannel layers grown by 5 h-long anodization experiments.

The Nb:O ratio for both as-formed and annealed oxide layers (0.29 and 0.33, respectively) is lower than that expected for stoichiometric Nb₂O₅ (i.e. 0.40). Also, the P2p photoionization (Fig. 4d) at 134.3 eV accounts for the presence of phosphates or similar P-containing species. Thus, it can be concluded that PO₄³⁻ species are adsorbed at the Nb₂O₅ nanochannel surface, and such species do not undergo desorption with annealing. It is possible that -PO₄³⁻ terminations contribute to the overall capacitance [49].

The Nb oxide nanochannel layers were grown to different thicknesses by 5, 12 and 24 h-long anodization, and were tested both as-formed (amorphous) and after crystallization as negative electrodes for supercapacitors in aqueous electrolytes.

The effect of the oxide crystallinity and annealing temperature was investigated by GCD measurements of sample anodized for 5 h – the results are compiled in Fig. 5a. It is evident that nanochannels annealed at 450 °C show enhanced capacitive behavior compared to amorphous structures and to structures annealed at 350 or 550 °C. Also, a pronounced IR drop is observed for the oxide layer annealed at 550 °C.

Figure 5

GCD measurements of (a) oxide layers anodized for 5 h and annealed at 350, 450 and 550 °C (in air, 1 h), and of (b) oxide layers anodized for 5, 12 and 24 h and annealed at 450 °C (in air, 1 h).

Fig. 5b shows the evolution of the capacitive behavior as a function of the anodization time (i.e. thickness of the Nb_2O_5 nanochannel layers) – based on the results in Fig. 5a, these structures

were crystallized at 450°C. Anodized oxide layers formed for 12 h show deliver the highest capacitance and the smallest IR drop.

It is evident that annealed Nb₂O₅ nanochannel layers outperform the as-formed (amorphous) counterparts, owing to their crystalline structures and better electron conductivity. However, the different capacitance values determined for oxide layers annealed at different temperatures cannot be explained in terms of crystallographic phase composition – please note that the Nb₂O₅ nanochannels are in any case converted into orthorhombic phase.

Figure 6

High- and (insets) low-magnification top-view SEM images of as-formed and annealed (350-550°C, 1 h, in air) Nb₂O₅ nanochannel layers grown by 5 h-long anodization experiments. The red arrows indicate the cracks formed in the oxide layer by annealing at 450°C.

However, in depth SEM analysis of the different samples reveals that the oxide layers undergo significant morphological changes when increasing the annealing temperatures. A first

difference is clear from the top view images in Fig. 6. While at the nanoscale (low-magnification images in the insets) the layers look virtually identical, one can see that annealing at 450°C leads to the formation of a few small cracks in the oxide layers (indicated with red arrows). Furthermore, wider and longer cracks form at 550°C.

It is worth mentioning that oxide layers annealed at 550°C were also found to delaminate (detach) from the electrode substrate after repeated electrochemical measurements. This can indicate that the cracks undermine the mechanical stability of the oxide electrode. Thus, a most plausible cause for the low capacitance can be ascribed to poor connection between the oxide and the metal back contact. Cracks within the Nb₂O₅ nanochannel layers (i.e. discontinuities within the electrode) or at the oxide/metal interface can also limit the electron conductivity.

This is clear from the SEM images in Fig. 7a, which show ion milled cross-sectional cuts of as-formed and annealed Nb₂O₅ nanochannel layers grown by 5 h-long anodization experiments.

One can see that for as-formed structures (5h-af), only a barrier-type anodic oxide is present at the bottom of the nanochannel. Well in line with literature, the anodic barrier oxide is as thin as ~ 10-15 nm, owing to the low anodizing voltage (5 V) [42].

The situation is different for annealed samples. Annealing at 350°C (5h-350°C) leads to the formation of thermal oxide at the nanochannel/metal substrate interface. Nevertheless, the thickness of such a layer (~ 55 nm) is still comparable to that of the anodic barrier oxide, and the formation of the thermal oxide has no impact on the morphology and mechanical robustness of the Nb₂O₅ nanochannel layer. Please note that these samples (5h-af and 5h-350°C) show the smallest IR drop (data in Fig. 5a).

Figure 7

(a) SEM images of ion milled cross sectional cuts of as-formed and annealed (350-550°C, 1 h, in air) Nb₂O₅ nanochannel layers grown by 5 h-long anodization experiments. Insets: high-magnification images of the Nb₂O₅ nanochannels and of the interface between the nanochannels and the underneath layer. (b) Thickness of the anodic barrier oxide (for as-formed nanochannels) and of the thermal oxide (for annealed nanochannels) as function of the annealing temperature.

Contrarily, the thermal oxide that forms upon annealing at 450°C (5h-450°C) is as thick as 11 µm, and several cracks form within the thermal oxide.

The thermal oxide thickness further increases up to 70 μm , when the Nb_2O_5 nanochannel layers are annealed at 550°C (5h-550°C). Worth noting is that in this case several cracks form also in the nanochannel layer (this is in line with results in Fig. 6).

Therefore, morphology and thickness of the formed thermal oxide (see a summary in Fig. 7b), and morphological deterioration of the nanochannel layer, can explain the different electrochemical capacitance response of the electrodes. In other words, on the one hand crystallization (annealing) is required to improve crystallinity and electron conductivity of the Nb_2O_5 nanochannel layers and, on the other hand, the annealing temperature should not exceed 450°C to prevent cracking and delamination of the oxide electrode. Annealing at 450°C can thus be regarded as an optimized condition in terms of a trade-off between the above-mentioned factors, which leads to best electrochemical performance.

A thermal Nb oxide layer was prepared as reference material by heat treating a non-anodized Nb foil. The formed thermal oxide (at the surface of the Nb metal foil) shows only a poor capacitance (Fig. S1). This comparison confirms that the higher capacitance of the anodic films can be attributed to the nanochannel morphology and directional electron conductivity. Nevertheless, it is expected that even higher performances could be reached by preventing the thermal oxide formation. This aspect could be tackled e.g. by growing Nb_2O_5 nanochannels on a different conductive substrate that does not deteriorate upon annealing.

The effects of the anodization time on the capacitance behavior (data in Fig. 5b) are minor compared to that observed for different crystallization temperatures. However, one can see that the capacitance scales (increases) with the thickness of the Nb_2O_5 nanochannel layers, and that layers grown by a 12 h-long anodization ($\sim 8 \mu\text{m}$ -thick) deliver the highest capacitance. In principle it is expected that thicker Nb_2O_5 nanochannel layers could deliver higher capacitance. Nevertheless, anodization times longer than 12 h lead to thinner anodic layers (due to etching)

and layers grown by a 24 h-long anodization ($\sim 5 \mu\text{m}$ -thick) show lower capacitance compared to those grown by a 5 h-long anodization ($\sim 3.6 \mu\text{m}$ -thick) – this is probably due to the collapse of the nanochannel structure at the layer top, which may limit the diffusion of the electrolyte deep into the nanochannels (i.e. lower electrode active area and slower kinetics – see Fig. 2b). In order to better understand the difference in electrochemical performance, the samples were characterized by CV and GCD measurements. Results for the best performing electrode (12h-450°C) are presented in Fig. 8 (data for the other electrodes can be found in the supplementary information (Fig. S2)).

Figure 8

CV and GCD of 12h-450°C at different (a) scan rates and (b) current densities, respectively; (c) rate capability of all the samples, and (d) stability of 12h-450°C up to 1500 cycles.

Fig. 8a shows the CV curves (for 12h-450°C) measured at different scan rates. The absence of clear redox peaks and the quasi-rectangular features confirm the capacitive electrode behavior, which could either originate from double layer formation and/or from capacitive faradaic redox reactions, also known as pseudocapacitance. The quasi-rectangular features of the CV also indicate that active metal centers of the Nb₂O₅ undergo successive redox reaction in the entire potential window [50]. This could be attributed to the cumulative effect from the reversible surface redox reactions and intercalation/deintercalation of cations (H⁺ or Na⁺) throughout the active nanochannel structure [32]. The possible Nb oxidation state changes during the redox processes in the aqueous 1 M Na₂SO₄ solution can be:

These processes at the electrode/electrolyte interface could be explained by the reaction in eq. 2 (below), where either cation fast adsorption/desorption process on the surface or intercalation/deintercalation throughout the active material are responsible for charge storage [32]:

The increase in the current densities with increasing the scan rate observed in the CV curves suggest that the nanochannel morphology supports a fast and reversible charge transfer and cation diffusion. These results also indicate the good rate capability of the material. When comparing the CV features of 12h-450°C (Fig. 8a) and 5h-450°C (Fig. S2a), it becomes clear that the later shows a more resistive behavior. Please note that for both electrodes the thermal oxide is ca. 11μm, while the anodic nanochannel layers are as thick as 8 and 3.6 μm,

respectively. Therefore, the resistive behavior of electrode 5h-450°C is possibly due to its higher thermal-oxide-to-active-nanochannel-layer thickness ratio (Fig. 2b and 7b).

The CV feature of 24h-450°C (fig. S2c) is similar to 12h-450°C although the former delivers lower current density. The main reason why the 24h-450°C electrode is less active than 12h-450°C is that the long anodization time (24 h) leads to corrosion of the outermost part of the oxide layer. The change in morphology (and chemistry) of the Nb₂O₅ nanochannel can thus be detrimental to electrolyte diffusion (deep in the electrode nanopores) and to charge transport/collection.

More generally, it is worth noting that the current response for 12h-450°C in the potential window of -1.3 to -0.5 V is higher compared to the current response in potential window of -0.5 to -0.2 V (CV in Fig. 8a). This suggests that the reversible redox reaction and/or intercalation/deintercalation processes are more favorable in the lower potential window, while the relatively low current response in the higher potential window could derive from double layer contribution or surface based redox reaction.

GCD measurements were carried out at different current densities to assess the effects on the capacitance, rate capability, and stability of Nb₂O₅ electrodes. GCD data of 12h-450°C are presented in Fig. 8b, and those for the samples 5h-450°C and 24h-450°C are in Fig. S2 b,d. Charge discharge behavior of electrode 12h-450°C, at all current densities, is symmetrical with a high average coulombic efficiency of 96% (calculated on the ratio of discharge and charge time). This testifies the reversibility of the electrochemical processes at the interface as well as the superior capacitive response of the Nb₂O₅ nanochannel electrodes. All GCD curves have two clear regimes (slopes); one is linear and takes place in the lower potential window. The second, in the higher potential window, show a steep decreasing trend. The linear charge and discharge behavior in the lower potential suggest the dominance of pseudocapacitive behavior

originating from reversible redox reaction and intercalation/deintercalation processes. In line with the CV results, the steep decreasing trend in the GCD data observed at higher potential can be caused by double layer capacitance. The fact that these two processes happen at different time scale could explain such a change in the slope [4-6]. The specific capacitance values of all the samples were calculated from the GCD plots at different current densities by using equation 3:

$$C_s = \frac{J \Delta t}{\Delta V} \quad (\text{eq. 3})$$

Where, C_s is the areal capacitance (mF cm^{-2}), J is the current density (mA cm^{-2}), Δt is the discharge time (s) and ΔV is the potential window. The capacitance values calculated for the different samples are reported in Fig. 8c. The maximum specific capacitance value, i.e. 100.1 mF cm^{-2} was obtained for 12h-450°C, while the electrodes 5h-450°C and 24h-450°C reached a capacitance of 98.57 and 73.71 mF cm^{-2} , respectively (measured at a current density of 1 mA cm^{-2}). The electrode 12h-450°C also shows the best rate capability and retains 63% of the initial specific capacitance at current density of 10 mA cm^{-2} . Particularly the electrode 5h-450°C shows a more pronounced drop in rate capability and retains only 46% at a current density of 5 mA cm^{-2} . The superior specific capacitance and remarkable rate capability of electrode 12h-450°C can be attributed to the open nanochannel morphology, to their crystallinity and increased conductivity, and at the same time to a minimized thickness of the thermal oxide formed at the nanochannel/metal interface.

In the current literature most of the Nb_2O_5 structures and composite materials developed thereof are studied as anode in organic electrolyte, while only few studies explore their use in aqueous system [26, 33, 35, 38, 51-55]. For the sake of comparison, worth mentioning is the work of Idrees et al. who reported for the first time that T- Nb_2O_5 in aqueous electrolyte ($1 \text{ M Na}_2\text{SO}_4$) could deliver a specific capacitance of 328 F g^{-1} at scan rate of 2 mV s^{-1} when tested in potential

window of 0-1.2 V [54]. Recently, Wang et al. synthesized MnO₂ nanosheet-decorated T-Nb₂O₅ nanorods on carbon cloth. This composite was tested in 1 M Na₂SO₄ electrolyte as positive electrode and delivered a specific capacitance of 319 F g⁻¹ at 0.2 A g⁻¹ [33]. Besides, there are to the best of our knowledge no reports of Nb₂O₅ tested in aqueous electrolyte in the negative potential window. We suggest therefore that our results pave the way for the use of Nb₂O₅ as negative electrode in aqueous electrolyte, thus avoiding the use of organic electrolytes and eliminating inherent disadvantages such as their relatively high cost, high flammability, and environment unfriendliness.

The stability of the electrode material is of prime concern for its practical applications. The electrode 12h-450°C was therefore subjected to a stability test; GCD measurements were carried out for 1500 cycles at a current density of 1.3 mA cm⁻². The electrode retains around 81% of the initial capacitance. This result can once more be ascribed to the morphology of the open and vertically aligned nanochannels (that allows an easy access of ions throughout the electrode surface), as well as to their chemical stability and inertness.

Kinetic analysis was carried out for the best performing electrode (12h-450°C). It is known that the total capacitance of a material takes into account contribution from the double layer, faradaic processes (which includes reversible redox processes at electrode/electrolyte interface), intercalation/deintercalation processes and bulk diffusion controlled processes. The presence of these different mechanisms of charge storage can be identified and differentiated from others by analyzing the CV data at different scan rates according to equation (4) and the information can be obtained by plotting log (*J*) vs log (*ν*) as function of potential:

$$J = a\nu^b \quad (\text{eq. 4})$$

In eq. (4), *a* and *b* are variable parameters and the measured current (*J*) obeys the power law function with scan rate (*ν*). When *b* values are close to one, the current response is

predominantly capacitive in nature and for the diffusional controlled processes the current flow at any given potential is expected to vary with the square root of the scan rate and in this case b equals to 0.5.

Figure 9

Kinetic analysis of the electrode 12h-450°C; (a) power law dependence of current (j) vs. the sweep rate (ν). The two curves show the variation of j with respect to ν at a potential of -1 V ($b = 0.79$), and at -0.3 V ($b = 0.99$); (b) b -values as a function of the potential for different sweep rate (anodic current taken into account); (c) Q vs. $\nu^{-1/2}$ and (d) Q^{-1} vs $\nu^{1/2}$.

b -values were accessed by plotting $\log(j)$ versus $\log(\nu)$ for different potentials. The plotted values according to eq. (4) give rise to a straight line with slope equals to b . For instance, the

plots of $\log(J)$ versus $\log(v)$ at applied potentials of -1 V and -0.3 V are illustrated in Fig. 9a, showing nearly a linear behavior and presenting different b values of 0.79 and 0.99, respectively. The distinct b values obtained at different potentials are plotted in Fig. 9b. In the higher potential range (mainly in the -0.3 – -0.5 V range), the average b values are higher than 0.95. A b value close to 1 in this potential range indicates that the current response arises primarily from double layer formation or fast reversible surface redox reaction i.e. pseudocapacitance. In the mid potential window (from -0.6 to -0.9 V), the variation in the current at different scan rate displayed b values in the range of 0.8 to 0.9 (average 0.85), that account for the occurrence of processes that are faster than the diffusional controlled ones and slower than double layer charge storage phenomena. This could be attributed to the facile intercalation/deintercalation processes, which are generally faster than diffusional controlled ones and slower than double layer or surface redox processes [4-6, 56]. The absence of diffusional controlled processes could be attributed to the morphology of the vertically oriented nanochannel layers that leads to easy access for the ions throughout the active surface area. This could also be one reason for the good rate capability obtained for the electrode 12h-450°C. b values in lower potential windows are close to 0.5 indicating the presence of diffusion controlled processes. The results obtained for the b -values at different potentials explain the current variations in the CV and potential changes in GCD plots.

After observing the presence of different charge storage processes by applying the power law equation, the charge storage processes were further studied (using an approach reported elsewhere [57]) to differentiate the charge storage contribution from double layer/fast surface based redox processes and intercalation/deintercalation-diffusional controlled processes from the total charge storage. The relationship between the charge (Q [coulomb]) and the scan rate of CV as described by the model is given below in eq. (5) and eq. (6):

$$Q = Q_{v=\infty} + \text{constant}(v^{-1/2}) \quad (\text{eq. 5})$$

$$Q^{-1} = Q^{-1}_{v=0} + \text{constant}(v^{1/2}) \quad (\text{eq. 6})$$

where, $Q_{v=\infty}$ is the surface adsorption charge corresponding to the voltammetric charge at $v = \infty$ and the value at $v = 0$ corresponds to the total stored charge denoted as $Q_{v=0}$. Therefore, by plotting Q versus $v^{-1/2}$ and Q^{-1} versus $v^{1/2}$ using eq. (4) and eq. (5), the surface adsorbed capacitance and total capacitance can be determined respectively from the y-axis intercepts. Both the plots are illustrated in Fig. 9 c,d. The results reveal that the contribution from the surface adsorbed double layer or from fast reversible surface based redox reactions is around 36% and the remaining capacitance, i.e. 64%, comes from intercalation/deintercalation or diffusional controlled processes. However, the b values determined at different potentials reported in Fig. 9b indicate that both the diffusion of cations to the bulk and intercalation/deintercalation processes take place.

Figure 10

EIS measurement for different samples. Nyquist plot (a) (inset: magnified view); Bode plots (c & d).

Table 2

Sample	R_s ($\Omega.cm^2$)	R_{ct} ($\Omega.cm^2$)	R_{total} ($\Omega.cm^2$)	W_o		χ^2
				($\Omega.cm^2$)	n	
5h-450°C	3.66	0.7	4.36	1.49	0.46	$1.6*10^{-4}$
12h-450°C	3.23	0.46	3.7	0.87	0.45	$2*10^{-4}$
24h-450°C	3.95	0.6	4.55	1.58	0.47	$1.4*10^{-4}$
12h-450°C 1500 cycles	5.33	0.5	5.83	2.46	0.4	$2.3*10^{-4}$

In order to further study, the electrochemical behavior of the Nb_2O_5 electrodes, electrochemical impedance spectroscopy measurements were carried out. The measurements were performed at OCP. EIS spectra of different samples are shown in Fig. 10. In order to acquire information such as ESR and Warburg resistance, the curves were fitted from high to mid-frequency range and the obtained results are compiled in Table 2. The charge transfer resistance for the electrode 12h-450°C is the lowest (total resistance of $3.23 \Omega.cm^2$) compared to other samples; the resistance measured for the electrodes 5h-450°C and 24h-450°C are 4.36 and $4.55 \Omega.cm^2$, respectively. The higher charge transfer resistances of the electrode 5h-450°C ($0.7 \Omega.cm^2$) could be due to the higher thermal-oxide-to-active-nanochannel-layer thickness ratio, as discussed above. On the contrary, the low charge transfer resistance of the electrode 12h-450°C confirms that the chosen anodization time and annealing temperature enabled a maximized capacity behavior.

Also, the Warburg resistance, which generally arises due to the presence of diffusional processes, is $0.87 \Omega \cdot \text{cm}^2$ for the electrode 12h-450°C and is clearly lower compared to other samples. The lower charge transfer and Warburg resistance could be one reason for the improved capacitive behavior of electrode 12h-450°C. However, the resistance and change in the phase angle in the low frequency region for all the samples appear to be similar as shown in Fig. 10 b,c.

The change in the impedance nature after 1500 cycles for 12h-450°C was also investigated. The fitted EIS data show an increase in the total resistance to $5.83 \Omega \cdot \text{cm}^2$ compared to the initial value of $3.7 \Omega \cdot \text{cm}^2$ and an increase of the Warburg resistance from $0.87 \Omega \cdot \text{cm}^2$ to $2.46 \Omega \cdot \text{cm}^2$. A drop in the phase angle on cycling can also be observed. The increased resistance upon cycling can be due to the cracking of nanochannel layers or to partial deterioration/collapse of the structure.

Conclusions

In this work Nb metal substrates were anodized in pure molten *o*-H₃PO₄ under self-organizing electrochemical conditions to grow Nb₂O₅ nanochannel layers of various thicknesses. These Nb₂O₅ nanochannel layers are supported by the Nb metal substrate and are therefore ready for use in electrochemical application. These layers were annealed under different conditions to tune their capacitive response, and were tested in aqueous 1 M Na₂SO₄ electrolyte in negative potential window between -0.2 to -1.25 V vs. SCE. An anodization time of 12 h and annealing temperature of 450°C led to 8 μm-thick orthorhombic Nb₂O₅ nanochannel layers that delivered improved electrochemical performance compared to electrodes prepared under other experimental conditions, reaching a specific capacitance of $\sim 100 \text{ mF cm}^{-2}$ at a current density of 1 mA cm^{-2} . These structures also showed remarkable rate capability and stability of 63% of

the initial capacitance at 10 mA cm^{-2} and 81% after 1500 charge-discharge cycles, respectively. Kinetic analysis of the electrochemical results revealed the occurrence of pseudocapacitive and diffusional controlled processes. EIS spectroscopy evidenced the lowest resistance of the electrodes compared to other experimental conditions, which is mainly due to the defined nanochannel morphology (high active area) of the Nb_2O_5 electrodes, to their crystalline nature and to a consequently minimized resistance across the electrode and at the electrode/substrate interface. The promising supercapacitive behavior in aqueous electrolyte in negative potential window suggests that the anodic Nb_2O_5 nanochannel layers have considerable potential as negative charge storage electrodes for pseudocapacitor applications.

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