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## **Electrochemical investigations of Nb<sub>2</sub>O<sub>5</sub>/carbon materials from filter paper, microfibrillated and bacterial celluloses by sustainable reductive mineralization.**

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### **Abstract:**

Cellulose is an attractive reagent for the elaboration of C-containing materials, but here, we also considered it as an O-provider for preparing macro, micro and nano-fibrous Nb<sub>2</sub>O<sub>5</sub>/C composites by a new mineralization with Nb<sub>2</sub>Cl<sub>10</sub> in anhydrous conditions. Our study highlights differences of reactivity between filter paper, microfibrillated or bacterial cellulose in connection with the crystallinity and the accessibility of the hydroxyl groups. The Nb<sub>2</sub>O<sub>5</sub>/C ratio was found to be adjustable (55-75% of Nb oxide) depending on the cellulosic precursor. Our composites were tested as electrodes that could be used as negative electrode in hybrid lithium-capacitor. Electrochemical characterizations of Nb<sub>2</sub>O<sub>5</sub>/C composites are reported and it was demonstrated that characteristics of the starting cellulosic reagents that influence physico-chemical properties of composites thus impact electrodes performances. Very interestingly, for 1C charging/discharging rates, capacities as good as thus of literature (150 mAh g<sup>-1</sup>) were obtained using our new sustainable synthesis protocol.

### **Introduction**

Electrode materials, used in energy storage devices such as batteries and supercapacitors, must now be designed at the nanoscale using green chemistry processes as much as possible [1]. Recently, semiconductor oxides like Nb<sub>2</sub>O<sub>5</sub> and its composites that could be used for electrochemical applications, but also in catalysis, photocatalysis, field emission, photovoltaic, photodetector, sensor and as electrochromic material, attracted many interest [2-4]. Looking at electrochemical energy storage, Bard et

al. first demonstrated that Nb<sub>2</sub>O<sub>5</sub> exhibits lithium and proton insertion [5, 6]. Compare to other possible materials for negative electrodes in hybrid-capacitors, Nb<sub>2</sub>O<sub>5</sub> has a high theoretical capacity of ~200 mA h g<sup>-1</sup> (*i.e.* higher than Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and TiO<sub>2</sub>, ~170 mA h g<sup>-1</sup>) which would be effective for improving the energy density. Moreover, unlike commercial Li-ion-capacitors made using graphite, Nb<sub>2</sub>O<sub>5</sub>-based electrodes work in a voltage range free of potential safety problems associated with electrolyte decomposition, resulting in a stable and very long cycle life. Finally, prelithiation of negative electrode materials, which could be necessary to reach high energy density with fair cycling performance, are not required for Nb<sub>2</sub>O<sub>5</sub>-based electrodes [7-10].

For Nb<sub>2</sub>O<sub>5</sub>, the electrochemical performance is closely related to its crystal structure, which can be amorphous, pseudo-hexagonal (TT-), orthorhombic (T-), tetragonal (M-) or monoclinic (H-). Briefly, Nb<sub>2</sub>O<sub>5</sub> orthorhombic (T- Nb<sub>2</sub>O<sub>5</sub>) crystalline phase have been shown to perform better than pseudo-hexagonal (TT- Nb<sub>2</sub>O<sub>5</sub>) or amorphous phase [7, 9, 11]. The excellent capacity and rate performance of nanostructured T-Nb<sub>2</sub>O<sub>5</sub> have been attributed to the easy Li insertion along favoured crystallographic pathways and open channels of interconnected NbO<sub>x</sub> sheets, leading to reduced energy barriers and improved local charge transfer in the structures [7-9, 12, 13].

The morphology, at the nanoscale, is the second key criterion according to Dunn *et al.* [8, 9]. Like for other metal oxides, carbon has been assembled with niobium pentoxide with two aims. The first aim is to improve the poor electrical conductivity of Nb<sub>2</sub>O<sub>5</sub> ( $\pm 3 \cdot 10^{-6}$  S cm<sup>-1</sup>). This can be done by combining Nb<sub>2</sub>O<sub>5</sub> nanoparticles with conductive scaffolds of carbon nanotubes [14-16], graphene [17], reduced graphene oxide [18], or carbide-derived carbon [19, 20]. Secondly, the sintering of Nb<sub>2</sub>O<sub>5</sub> nanoparticles is detrimental because of specific surface area decreasing which can occur during the thermal treatment that is necessary for T-Nb<sub>2</sub>O<sub>5</sub> formation (> 600°C). To prevent this, a Ta-substitution was proposed in the literature to achieve stabilized Nb<sub>2</sub>O<sub>5</sub> polymorph [21]. However, wrapping nanoparticles with carbon coatings appears to be the easiest way to prevent this phenomenon.

Different approaches have been investigated to do this, such as polymer templated sol-gel processing of niobium oxide precursors in which the polymer (Igepal CO-520 [22], PEO-*b*-PS[23-26], is converted into carbon upon pyrolysis. In hydrothermal processes, resorcinol/formaldehyde [17, 27], sucrose [28] and glucose [29], have been used as a water soluble source of carbon. Insoluble cellulose [30-32] or cellulose acetate [33, 34] were the first sacrificial templates used to control Nb<sub>2</sub>O<sub>5</sub> particle growth. In terms of fibers, pure Nb<sub>2</sub>O<sub>5</sub> polymorphe and Nb<sub>2</sub>O<sub>5</sub>/C composite have been prepared respectively by electrospinning of sol-gel solution mixed with polyvinylpyrrolidone as carrier [35, 36] or electrospinning of powder of Nb<sub>2</sub>O<sub>5</sub> mixed with polyvinylalcohols as carrier [37]. Recently, graphene

[38], reduced graphene oxide [39, 40] or carbon microspheres [27] were used to synthesize Nb<sub>2</sub>O<sub>5</sub>/C composites but these approaches suffer from lack of scalability. On the other hand, cellulose has recently been the focus of renewed attention and, for example, insoluble nanocrystals were used as a template for the development of Nb<sub>2</sub>O<sub>5</sub> composites prepared by a sol-gel route but in that case reactivity of cellulose was not engaged and even was not used a carbon-phase precursor [41].

Using a very innovative method, our approach to use cellulose for processing such metal oxides and metal oxide/carbon composites is very different. Recently we reported a new approach to limit solvent and reagent use, to work at low temperature while using the cheapest and greenest reagents. Completely differently from all the other previous work using cellulose, here, cellulose provides the oxygen required for metal oxide formation, and serves also as a carbon precursor for the metal oxide/carbon composite [42-45]. This allows to avoid any sol-gel process using solvent and solution chemistry. By this inexpensive, simple and as sustainable as possible process, we reported the mineralization of cellulose to obtain highly anisotropic morphologies like nanoplates, needles and flowers. Their formation is apparently linked to the reactivity of cellulose and similar morphology has never been reported when cellulose is combined with the sol-gel route to metal oxides. Moreover, for example, in the case of TiO<sub>2</sub>/C, a deposit of a few nanometers of carbon on metal oxide nanoparticles was evidenced. These data prompted us to consider that this process could be a possible route to obtain new efficient Nb<sub>2</sub>O<sub>5</sub>/carbon nanocomposites.

Thus, we report in this article the first study that highlights the possibility offered by cellulose for preparing metal oxide and metal oxide/carbon composite investigating Nb<sub>2</sub>O<sub>5</sub> as the metal oxide due to its attractive properties, especially for electrochemical applications. Nb<sub>2</sub>O<sub>5</sub>/C nanocomposites were prepared using new route that we have developed, and the effect of the cellulose morphology crystallinity and size were studied. We found that Nb<sub>2</sub>O<sub>5</sub>/C nanocomposites prepared using micro-fibrillated cellulose (MFC) allowed preparing electrodes with capacity of more than 150 mAh g<sup>-1</sup> at 1C that exhibits same performances than the literature but prepared with much more complex procedures.

## Experimental

*Materials.* Diniobium(V) decachloride (Nb<sub>2</sub>Cl<sub>10</sub>) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) are of analytical grade from Across (France). Dichloromethane was freshly distilled over P<sub>2</sub>O<sub>5</sub> before used. Filter paper FP-3-101-090 is from Sartorius (France). Aerogel of micro-fibrillated cellulose (MFC) was prepared by freeze-drying from *t*-butanol solvent exchanged suspensions according to the procedure previously described [46]. Aerogel of bacterial cellulose (BC) were prepared according to a previously reported procedure then

freeze dried from water solution [47]. All cellulosic materials were dried 3 days in an oven at 80°C just before use. All manipulations with Nb<sub>2</sub>Cl<sub>10</sub> and dried nanocellulose aerogel were performed in a glove box under argon atmosphere (<10 ppm of water).

*Instrumentation.* The X-ray powder diffraction (XRPD) patterns of the samples were recorded using a diffractometer (Philips X'Pert Pro, Netherlands). Raman spectra were obtained using Horiba LabRAM ARAMIS, Japan, with excitation wavelength of 633 nm. FT-IR were recorded on crushed powders with a Spectrum 2 (PerkinElmer) in ATR mode after accumulation of 16 scans. N<sub>2</sub>-physisorption isotherms were obtained at 77 K using Micromeritics Tristar, USA. The samples were outgassed for 12 h at 150°C under vacuum (2 Pa). The pore size distribution was calculated from the desorption branch using the BJH method. Thermogravimetric analyses (TGA) were obtained using Netzsch Simultaneous Thermal Analyser STA 409 PC Luxx and Setaram Labsys TGA-DSC. Scanning electronic microscopy (SEM) images were obtained with a Hitachi S-4800, Canada. Energy dispersive X-ray analysis (EDAX) was done using the EDAX attachment (Oxford Instruments, UK) of the SEM system.

*Preparation of NbO<sub>x</sub>@FP, NbO<sub>x</sub>@BC and NbO<sub>x</sub>@MFC.* In a glove box under inert atmosphere (< 2 ppm H<sub>2</sub>O), cellulose source (FP, MFC or BC), dichloromethane (30 mL), and Niobium(V) pentachloride were placed into a Teflon-lined autoclave (in quantities described in table S1), and placed in an oven at 85°C for 3 days. When cooled down to room temperature, black residue was washed with anhydrous dichloromethane (3 x 20 mL). Then, under ambient atmosphere, residues were subsequently washed with standard dichloromethane (3 x 20 mL), and dried in an oven at 80°C for 24 h. Sample obtained are named: NbO<sub>x</sub>@FP, NbO<sub>x</sub>@BC and NbO<sub>x</sub>@MFC, respectively according to cellulosic precursor used.

*Thermal treatments.* Pyrolysis under argon was performed at 800 °C, for 1 h, at a heating rate of 5°C min<sup>-1</sup>, yielding the corresponding samples called Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>, Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>, Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>, respectively.

*Electrochemical characterizations.* All electrochemical characterizations were performed in Swagelok® cell at room temperature on an MPG2 instrument from BioLogic by using Teflon-made Swagelok® cell. All electrodes were composed of the active material, acetylene black (as conductive additive) and carboxymethylcellulose (as binder) according to the following mass ratio: 80:8:12. After stirring in water, the mixture was spread uniformly onto a copper current collector using a 3540 bird film applicator from Elecometer leading to electrode thickness of about 150 μm. Lithium metal disks were used as both reference and counter electrodes, and Whatman glass fibers filters were used as separator. The electrolyte was 1 M LiPF<sub>6</sub> in a 1:1:3 solution of ethylene carbonate, propylene carbonate and dimethylcarbonate. All electrochemical results are provided taking into account the mass of the active material, *i.e.* the mass of

the Nb<sub>2</sub>O<sub>5</sub>/C composite. For galvanostatic measurements, the cells were charged and discharged at various C rates from 1 C to 1000 C (1 C corresponding to 100 mA g<sup>-1</sup>). For cyclic voltammetry, all cells were cycled at various scan rates ranging from 0.5 to 500 mV s<sup>-1</sup>.

## Results and discussion

In order to synthesize Nb<sub>2</sub>O<sub>5</sub>/C electrodes, the strategy that was chosen include a first mineralization step of the cellulosic precursor by Nb<sub>2</sub>Cl<sub>10</sub>, in anhydrous conditions followed by a calcination step to obtain the desired crystalline phase for the niobium dioxide.

*Mineralization of Cellulosic support by Nb<sub>2</sub>Cl<sub>10</sub> in anhydrous conditions.* A first interesting result is that, when mineralization was performed at 85°C, the recovered hybrid materials, either NbO<sub>x</sub>@FP, NbO<sub>x</sub>@BC and NbO<sub>x</sub>@MFC present shape and mechanical consistency with the starting cellulosic material, except the final colour that was black, and this whatever the type of cellulose used (Figure. S1). XRD experiments show that although they are broadened, similar signals than cellulose precursor, are observed in the corresponding hybrid samples before any thermal treatment (Figure. 1). Consequently, at 85°C, the crystal structure of cellulose is partially preserved. At that stage of the synthesis process, no niobium-containing inorganic crystalline phase could be identified. Materials from this mineralization process was actually deeply characterized and FTIR and Raman analyses can be find in supplementary information (Figures. S2 and S3). <sup>13</sup>C SS NMR was used to determine the crystallinity of samples and spectra are shown in figure 2. For all the samples, the spectra displayed features typical of native cellulose that have been already abundantly described in the literature in terms of allomorphic ratio and crystallinity. Bacterial cellulose BC sample exhibits mainly Iα phase and a high degree of crystallinity, whereas FP and MFC are predominantly Iβ, with intermediate and lower crystallinity, respectively. An interesting conclusion is that the reaction seems to have partially preserved the integrity of the crystalline organization of the initial substrate, known to be sensitive to thermal or chemical transformation. Degree of crystallinity of the samples was determined by integrating the C4 signals from the crystalline (between 86 and 92 ppm) and the disordered contributions (between 80 and 86 ppm). The results give crystallinity indices of 0.57 for MFC, 0.65 for FP and 0.82 for BC. This is in good agreement with the fact that the elementary nanocrystals are smaller in MFC, of intermediate size for FP and even bigger in BC, so that the surface to volume ratio is lower for bacterial cellulose. For, composites, NbO<sub>x</sub>@FP, NbO<sub>x</sub>@MCF, NbO<sub>x</sub>@BC, integrations of these contributions represents a molar fraction of 0.11, 0.08 and less than 0.02 for MFC, FP and BC respectively. This is in good agreement with the results obtained on the crystalline and disordered contributions, showing that the consumption of cellulose is directly

proportional to the amount of hydroxyl exposed at the surface, and hence on the crystallinity of the sample.

The second step of the process is to calcinate the  $\text{NbO}_x\text{@FP}$ ,  $\text{NbO}_x\text{@BC}$  and  $\text{NbO}_x\text{@MFC}$  to obtain the desired  $\text{Nb}_2\text{O}_5/\text{C}$  composites. X-ray diffraction experiments as a function of the temperature was performed between ambient temperature and  $1100^\circ\text{C}$  and it was concluded that a heating to  $800^\circ\text{C}$  correspond to the optimal condition to obtain T- $\text{Nb}_2\text{O}_5$  without large crystallites. Indeed this structure is believed to be the most efficient considering the application of  $\text{Nb}_2\text{O}_5$  as material for electrochemical energy storage device) [7]. More details about these XRD experiments are available in supplementary information (Figure. S4 and table S2). In order to improve clarity of the discussion that follows, only samples prepared at  $800^\circ\text{C}$  are going to be considered in this manuscript.

*Structural characterization  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}$ ,  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}$  and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}$ .* At first, morphological and chemical characterizations were performed by SEM, TEM and EDX. SEM images (Figure. 3) show a good preservation of the fibrous structure of the starting cellulosic support (Figure. S5) and  $\text{Nb}_2\text{O}_5$  particles are visible at the surface of the carbon left by the carbonization. For sample  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}$  and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}$ , the assembly of  $\text{Nb}_2\text{O}_5$  nanocrystals and carbonaceous network is homogeneous at the nanoscale. For sample prepared with FP, the situation is less homogeneous, big pieces of carbonaceous residue being mixed with micro and sub-micrometer particles of niobium oxide. An EDX mapping of the elements confirms a complete and homogenous covering of C, O and Nb for all the samples, and an example is given for  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}$  in figure S5. Figure 4 shows HRETM images for the most performant material (see below)  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}$  to better understand its nanostructure. At the lowest magnification, a micro- to nano-fibrillated structure is observed in good agreement with MEB analyses. Some separated aggregates of inorganic nanoparticles are present but the major part of the material is made of nanoparticles of  $\text{Nb}_2\text{O}_5$  (20-50 nm) well dispersed along the carbonaceous fibrils (Figure 4B, C and D). This is confirmed by EDX analysis showing that, spotting on large zone ( $> 100$  nm) evidences the presence of C, Nb and O (Figure S6). At higher magnifications, in small dark low-density zones ( $< 20$  nm) only C is detectable along with O, although with much lower intensity for this latter. At the opposite, high-density zones exhibit high intensity for rays of Nb and O, however, C rays is also clearly present although in lower intensity. This is in agreement with the images that reveals a highly disordered and poorly graphitized carbon layer of few nanometres thickness  $\approx 1\text{-}5$  nm covering the  $\text{Nb}_2\text{O}_5$  nanoparticles (Figure 4B, C, D and E).

A very important thing to evaluate the performance of the electrodes is to know the  $\text{Nb}_2\text{O}_5/\text{C}$  weight ratio. To do this, TGA analyses in air and in argon were performed and show weight losses starting in all

cases around  $\approx 100^\circ\text{C}$ , much lower than the one of the pristine celluloses ( $180\text{-}200^\circ\text{C}$ ) (Figure. S6). This is ascribed to elimination of adsorbed volatile compound and elimination of HCl arising from condensation/hydrolysis of residual Nb-Cl and Nb-OH (from mineralization). In air, elimination of the carbonaceous residue by combustion is complete by  $450^\circ\text{C}$ ; yields are reported in table 1. Under argon, the weight loss due to carbonization of the cellulosic residue occurs up to  $1000^\circ\text{C}$ , although it results to higher yields. Combining these TGA yields under air and argon and assuming that carbon results from the carbonization of cellulose, allows estimating the  $\text{Nb}_2\text{O}_5/\text{C}$  mass ratio of the different samples and they are summarized in table 1. Comparison of the samples shows that the proportion of carbon is the highest for samples prepared with FP ( $\sim 45\%$ ) and the lowest is for samples prepared from MFC ( $\sim 25\%$ ), the one for sample prepared from BC being in between around 30%. Interestingly this process give access to a proportion of carbon that is in-between the lowest one obtained with surfactant (Igepal® CO520 7% of C [22] and PEO-PS 11% of C) [23], and the highest obtained with saccharides and resins (sucrose 59-87% of C [28] and resorcinol-formaldehyde:70-75% of C[17]). The resulting amounts of carbon for the three precursors used, are in line with the results shown by SS-NMR. Our findings show a lower production of  $\text{NbO}_x$  for the more crystalline substrate and higher rates for the less crystalline, and hence more reactive substrates exposing a higher number of hydroxyl groups. This is an important result because it could open new opportunities for the tailoring  $\text{Nb}_2\text{O}_5/\text{C}$  composites containing predictable amount of oxide, and hence a ratio of carbon/oxide that can be finely tuned.

XRD measurements after bulk pyrolysis (Figure. S7) allowed the determination of the crystallographic structure and the evaluation of the crystallite's size.  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}$  presents a mix of two phases: an orthorhombic T- $\text{Nb}_2\text{O}_5$  (ICSD 30-0873,  $2\theta = 22.6, 28.4, 36.5, 46.1$  and  $55.2^\circ$ ) and a tetragonal  $\text{NbO}_2$  (ICSD 76-0682,  $2\theta = 26.0, 35.2, 37.1, 40.0$  and  $52.0^\circ$ ), no quantitative ratio is proposed due to overlapping of signals. The T- $\text{Nb}_2\text{O}_5$  phase seems to be the most present, even if it has smaller crystallites (30 nm) than the  $\text{NbO}_2$  one (58 nm).  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}$  presents also a mix of  $\text{NbO}_2$  and  $\text{Nb}_2\text{O}_5$ , the latter being in major proportion. The crystallite sizes of the two phases are this time very close (25 and 24 nm, respectively).

Finally, it is necessary to know the surface area of our synthesized compounds as electrochemical surface area is directly related the performance of electrochemical devices. However, it is unfortunately a very difficult information to get, especially considering carbonaceous materials and oxides. Nevertheless, it is usual, and accepted, to consider the BET specific surface area to discuss morphological properties of the samples (porosity, external surface etc...). Nitrogen adsorption and desorption isotherms were recorded (Figure. S8) and BET surface area (total surface), the micrometric surface and the mesoporous surface



(also called external surface) were determined (Table 2). Composite obtained from FP and BC cellulose show similar characteristic with BET surface of about  $200 \text{ m}^2 \text{ g}^{-1}$  including  $50 \text{ m}^2 \text{ g}^{-1}$  of microporous area (25 %). Interestingly, MCF cellulosic reagent lead to the highest BET surface area ( $372 \text{ m}^2 \text{ g}^{-1}$ ) with a microporous surface of  $258 \text{ m}^2 \text{ g}^{-1}$  representing 70 % of the total surface. Specific surface area and especially pore size distribution are very important to keep in mind when looking at the electrochemical properties. Table 3 also summarize the total pore volume for the composites and the average pore size for samples obtained from three different cellulosic reagent.

*Electrochemical evaluation of the Nb<sub>2</sub>O<sub>5</sub>/C composites.* In this study, electrochemical characteristic of our Nb<sub>2</sub>O<sub>5</sub>/C composites were investigated using cyclic voltammetry and galvanostatic cycling and results are discussed in following paragraph. It is not the purpose of this study to claim that we present a real supercapacitors, but rather than we evaluate candidates that could be used as negative electrodes in an hybride Li-capacitor.

Cyclic voltammetry is a very convenient technic to study electrochemical behaviour of our composites. Figure 5a) shows the CVs for Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup> at the lowest scan rates. As, it is known, the peak current is related to the scan rate as expressed in the following equation (eq. 1) [7]:

$$i = av^b \quad (\text{eq. 1})$$

where  $i$  is the peak current (A),  $v$  is the scan rate ( $\text{mV s}^{-1}$ ) and  $a$  and  $b$  are adjustable variables. Particularly, the  $b$ -values gives precious information about electrochemical mechanism. A value of 0.5 indicates that process is purely diffusional whereas a value of 1 indicates a thin-film behaviour. A  $b$ -value between 0.5 and 1 would indicate a process that is governed by restricted diffusion [7]. Figure 6 shows the evolution of the current as a function a scan rate (logarithm scale).  $b$ -values can be extracted from the slopes that are observed. For our 3 cellulosic precursors, the general is the same. At lowest scan rates  $b$  is 0.7 for Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup> and Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup> and  $b$  equal 0.8 for Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>. When scan rate becomes more important slope decreases, a  $b$ -value reaches 0.5 in every cases. Two-well defined area can be observed. In a first one, at lowest scan rates, the process is governed by a restricted diffusion whereas when scan rate increases, process is governed by semi-infinite linear diffusion.

On the other hand, for this kind of pseudo-capacitive materials, it is usual to discuss the relative contribution of surface capacitive current and diffusion-controlled intercalation process [48, 49]. At a fixed potential, the current response, that allows to distinguish the two mechanisms is expressed according the following relation (eq. 2):

$$i(V) = k_1v + k_2v^{0.5} \quad (\text{eq. 2})$$

Where,  $k_1v$  is the current relative to surface capacitive effect and  $k_2v^{0.5}$  is the current relative to diffusion intercalation process. As explained in previous references, for analytical purpose the equation is rearrange and expressed as follows (eq. 3):

$$\frac{I(V)}{v^{0.5}} = k_1v^{0.5} + k_2 \quad (\text{eq. 3})$$

When  $I(V) v^{-0.5}$  is plot as a function of the square root of the scan rate,  $k_1$  and  $k_2$  can be quantified,  $k_1$  being the slope of the curve and  $k_2$  the y-axis intercept.

For all our device, independently of the type of cellulosic precursor used to synthesized the  $\text{Nb}_2\text{O}_5 / \text{C}$  composite, this separation between the two above-mentioned mechanisms was, in fact, impossible. This indicates that our materials never behave according to one or the other type mechanism. To prove this, the normalized current  $I v^{-0.5}$  was plot as a function of the potential (figure 5b). If process were governed by diffusion-controlled intercalation process, curves for different scan rates should overlap, at least at one potential. This is obviously not the case and this comfort the current peak analysis (figure 6) that showed that our process is a governed by restricted diffusion on the whole potential range and never exclusively governed by one of the particular case described above. However, and because it is an important point to discuss, capacitive contribution of the electrode, which can be attributed to carbon from the composite, have been estimated by integration of the area define by the lower and upper potential of the positive scan and the value of pure capacitive current determined at high potential versus  $\text{Li}^+/\text{Li}$  (around 2.7 – 2.8 V). For all CVs presented in figure 5a, capacitive contribution was found to be close to 20%. It is important to mention that this value, although low, is likely over estimated because, according to literature [48, 49] the capacitive contribution in the faradaic region should be lower than this taken into account to determine this value of 20%. Actually, even if carbon contribution cannot be considered as negligible, this proves that the storage performance of our electrode comes mostly from the  $\text{Nb}_2\text{O}_5$  pseudocapacitive material.

More than any, what is important in this study is the comparison and the discussion about the three new sustainable synthesis methods that allowed preparing  $\text{Nb}_2\text{O}_5/\text{carbon}$  composites. Cyclic voltammograms for the three different kinds of  $\text{Nb}_2\text{O}_5\text{-C}$  (from 3 different cellulose), are shown in figure 7. Both anodic and cathodic peaks are broad, but they flatten down as the sweep rate decreases. This is an expected

behaviour for these kind of intercalation materials. The comparison of the three samples shows an important difference between the specific currents measured on the different materials.  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}$  presents higher specific currents than the two other. This is consistent with physico-chemical characterisations which showed that synthesis with MCF cellulose leads to higher specific area, nicely dispersed  $\text{Nb}_2\text{O}_5$  particles, highest  $\text{Nb}_2\text{O}_5 / \text{C}$  ratio etc... It is important to notice that the poorest sample in terms of carbon ratio exhibits the best electrochemical performance versus lithium intercalation, proving that carbon contribution to the specific capacitance is almost insignificant compare to  $\text{Nb}_2\text{O}_5$  contribution. Moreover, fact that carbon does not explain capacitance values can be seen on CVs between 2.5 and 3.0 V vs.  $\text{Li}^+/\text{Li}$  where the “capacitive area” related to ion adsorption on carbon surface is very low compare to the niobium region between 1.2 and 2.5 V vs.  $\text{Li}^+/\text{Li}$ .

Another feature that have to be highlighted is that, if the peak shift is continuous for  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}$ , it can be noticed that, for the two other samples, the voltammograms with a sweep rate higher than  $200 \text{ mV s}^{-1}$  are almost stackable, with a disappearance of the two peaks. It suggests that, for  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}$  and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}$ , beyond  $200 \text{ mV s}^{-1}$ , the sweep rate is too fast for exchanging  $\text{Li}^+$  between the electrodes on the investigated potential window. These results highlight that different cellulosic precursors lead to different electrochemical behaviour and thus that performances of  $\text{Nb}_2\text{O}_5$  could be further optimized if a more suitable precursors were used.

Galvanostatic cyclings at different charging / discharging rates were performed on each sample and voltage profiles are presented in figure 8. 10 cycles were recorded for each rate and are all shown. As we can see, the ten cycles are almost stackable, which is very interesting particularly at high charging/discharging rates. This indicate a good stability even under fast sollicitation. After 20 cycles, each electrode reaches a coulombic efficiency higher than 99 %. Similarly, to the cyclic voltammetry, an important difference of performances can be observed between  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}$  and the two other samples. At c-rate of 1C,  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}$  presents a reversible capacity of  $\sim 150 \text{ mAh g}^{-1}$ , whereas  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}$  and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}$  ones are only close to  $70 \text{ mAh g}^{-1}$ . Another important feature is that the galvanostatic curves do not present any insertion plateau, which is characteristic of nanosized insertion materials and of a pseudo-capacitive behavior. In such systems, the specific area of the material is expected to have a great influence on electrochemical performances.

The specific capacity provided by  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}$ ,  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}$  and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}$  according to the C-rate (where C is set at  $100.8 \text{ mA g}^{-1}$  for one electron process) is presented in figure 8. Usually C-rate is a common metric for battery materials and not for supercapacitors. However, we decided to use it in order to match the data from Dunn et al publication which is the reference for  $\text{Nb}_2\text{O}_5$  [7]. For a better clarity,

each dot represents the capacity of the tenth discharge for the considered C-rate. As a comparison, values from Augustyn et al. (a) [7], Zhang et al. (b) [50] and Kong et al. (c) [41] are also given. For low C-rate capacity is as good as this of the reference publications indicating that our sustainable synthesis is very promising for pseudo-capacitor materials. The following decrease of the capacity of our materials is more pronounced than those of Dunn et al., what could be attributed to the presence of the less favourable NbO<sub>2</sub> phase in our samples. Further development on cellulosic precursors will permit to accommodate this issue. Once again, another notable feature is the difference of capacity between Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup> and the two other samples. This difference is consistent to the gap of specific area between the samples. indeed, for a charging/discharging rate of 1C, our best material, Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>800, exhibits a capacity of ~150 mAh g<sup>-1</sup> and it have a specific area of 370 m<sup>2</sup> g<sup>-1</sup>, compare with the ~70 mAh g<sup>-1</sup> and 200 m<sup>2</sup> g<sup>-1</sup> for Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>, the two samples having similar Nb<sub>2</sub>O<sub>5</sub>/C ratios (respectively 75 and 70 wt.% of Nb<sub>2</sub>O<sub>5</sub>). On the other hand, the capacity of Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup> is ~67 mAh g<sup>-1</sup>, and can be attributed to the combination of a lower content in Nb<sub>2</sub>O<sub>5</sub> (55 wt.%) and a higher specific area (245 m<sup>2</sup> g<sup>-1</sup>) than Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>. These results demonstrate unambiguously that our three composites possess the same intrinsic storage performances. However, as a very interesting finding, the Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup> synthesis allowed to double the electrochemical surface of Nb<sub>2</sub>O<sub>5</sub>-C materials and thus to double their capacity.

A very important thing that has to be noticed is that we did not performed prolonged cycling, at least in classic way, because we assume that our composites are still not optimized and it wouldn't be relevant to start time-consuming experiments in these conditions. However, figure 9 shows the evolution of the capacity as a function of the C-rate. For each charging / discharging rate, 10 galvanostatic cycles were recorded. As expected, capacity, decreases when solicitation becomes more important (time for charge and discharge becomes shorter). Actually, the very interesting thing is that after the solicitation at 1000C, when a charging / discharging C-rate of 1C is applied once again, the initial capacity is reached. The device has not only been cycled 180 times, (from 1C – to 1000C) but also with high solicitations (as high as 1000C). This clearly highlights that our materials can be cycles more than 200 hundreds times and at high charging/discharging rate without any loss of capacity.

These findings are very important because they open many opportunities to design new efficient Nb<sub>2</sub>O<sub>5</sub>/C composites to be used in hybrid supercapacitors from cheap precursors and using a sustainable process.

## Conclusions

The above set of results shows a new aspect of the reactivity of cellulose, the latter being directly dehydrated with the cheapest and greenest niobium reagent, niobium(V) chloride, at low temperature. Therefore, the resulting Nb<sub>2</sub>O<sub>5</sub>/C composites can be prepared by a simple and up-scalable protocol. It is highlighted that all the cellulosic fibers are not equivalent, indeed comparison of filter paper, bacterial cellulose and microfibrillated cellulose shows that the latter is the best for elaborating a homogeneous and performant nanocomposite, thanks to its low crystallinity, small size and, consequently, the low proportion of carbon that is left after pyrolysis. In relation with that, electrochemical properties, toward Li-intercalation, are in the range of those reported in literature to date and that prepared by much more sophisticated and expensive methods like hydrothermal or polymer templated approach. It is very encouraging to consider our synthesis as a new efficient way to prepare Nb<sub>2</sub>O<sub>5</sub>/C composites that could be tested as real negative electrode in a hybrid Li-capacitor. Considering that cellulose precursor allow tuning crystallographic structure, BET surface, microporosity, oxide/carbon ratio, morphology of oxide particles etc... our results highlight the benefit of our approach to develop new enhanced architecture for energy storage applications from natural polysaccharides.

### **Conflicts of interest**

There are no conflicts to declare

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### **Notes and references**

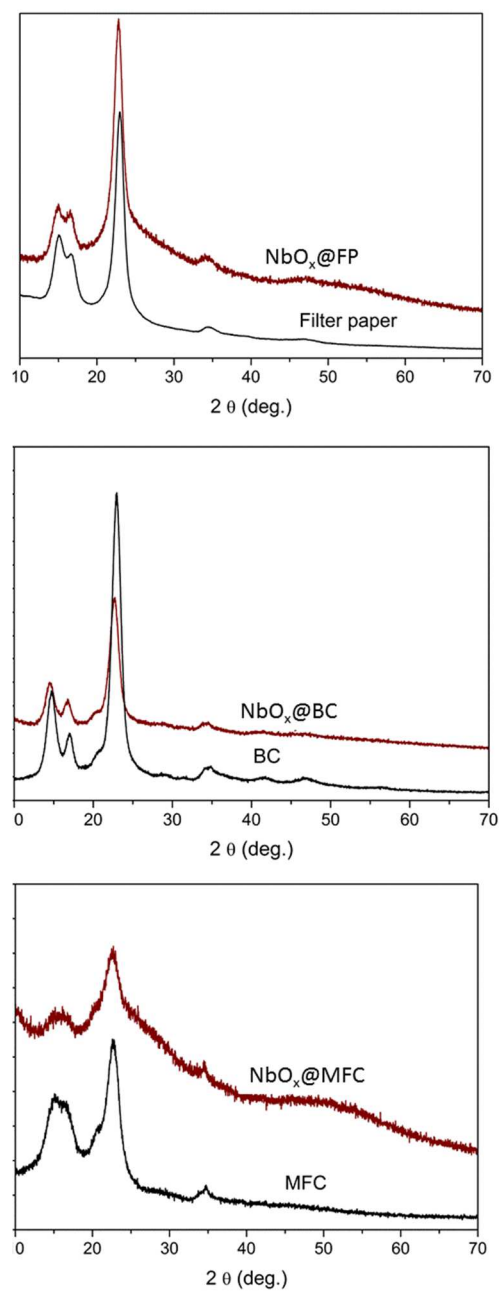
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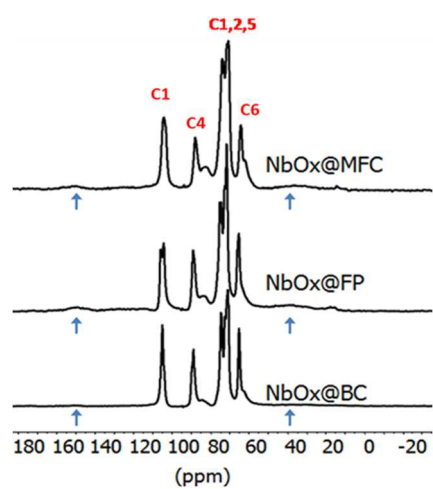
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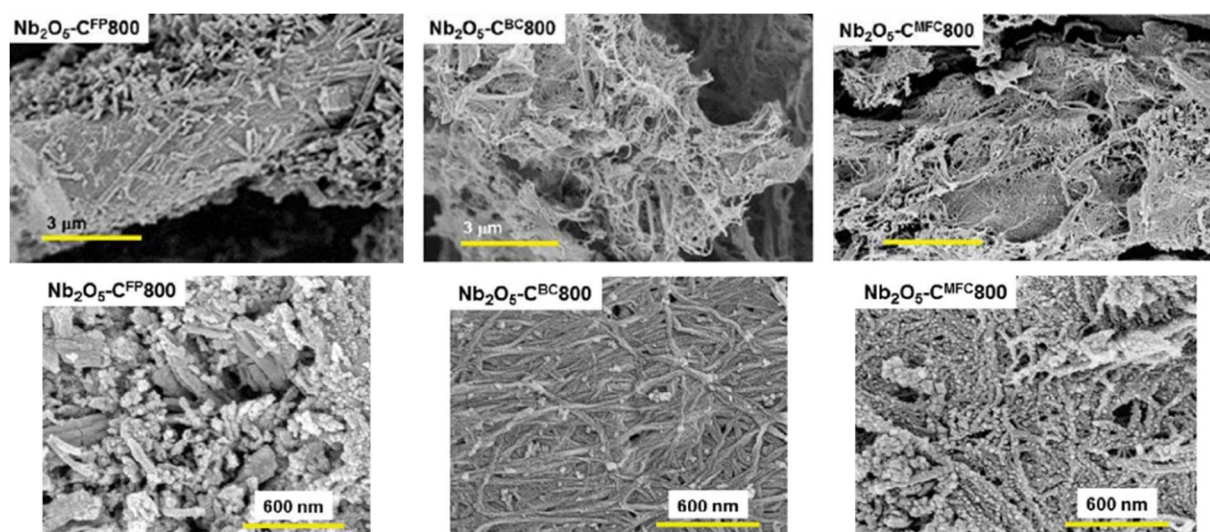




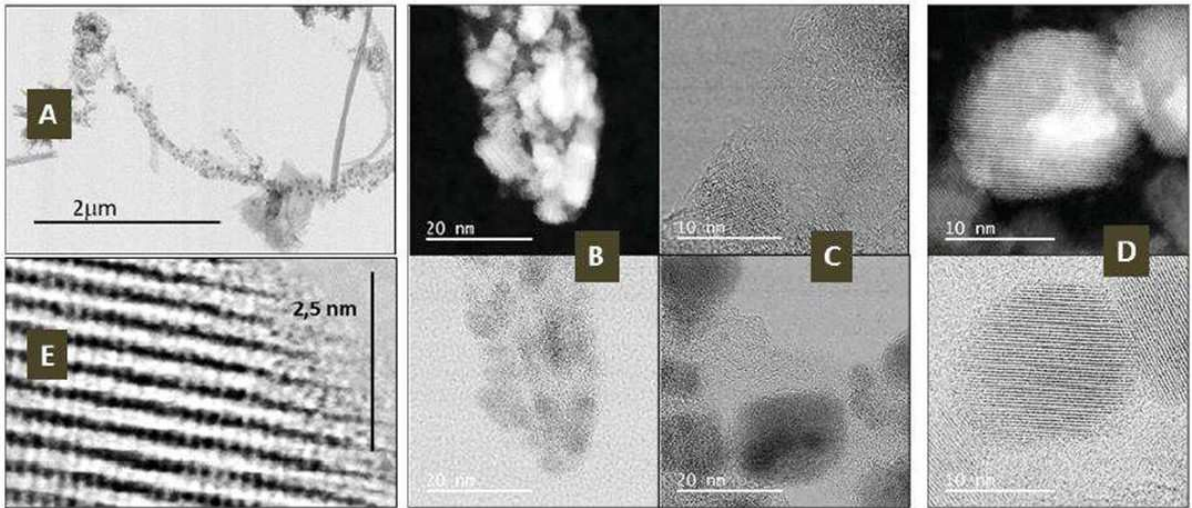
**Fig. 1:** X-ray diffraction patterns of cellulosic material (FP, MCF and BC) and the corresponding hybrid materials resulting from the mineralization process, respectively  $\text{NbO}_x@FP$ ,  $\text{NbO}_x@MCF$  and  $\text{NbO}_x@BC$ .



**Fig. 2:**  $^{13}\text{C}$  SS NMR of hybrid materials resulting from the mineralization process respectively  $\text{NbO}_x\text{@FP}$ ,  $\text{NbO}_x\text{@MCF}$ ,  $\text{NbO}_x\text{@BC}$ .



**Fig. 3:** SEM images magnifications of  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}800$ ,  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}800$  and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}800$  resulting from the pyrolysis under argon of  $\text{NbO}_x\text{@FP}$ ,  $\text{NbO}_x\text{@MCF}$ ,  $\text{NbO}_x\text{@BC}$ .



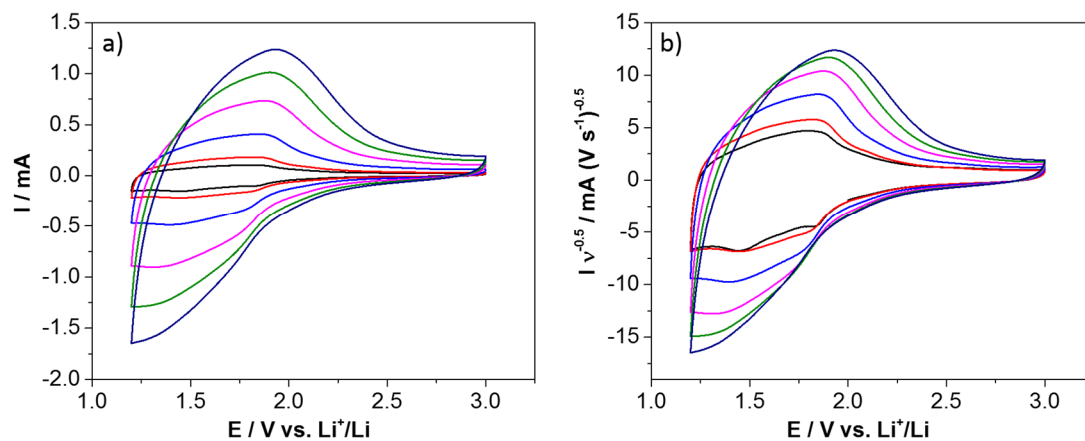
**Fig. 4:** HRTEM of  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}$  resulting from the pyrolysis under argon of  $\text{NbOx@MFC}$ .

Starting sample	Name &	Name	Name
	Yield at 1000°C <sup>a</sup>	Yield at 800°C <sup>b</sup>	Yield at 900°C <sup>b</sup>
	Nb <sub>2</sub> O <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub> /C ( % )	Nb <sub>2</sub> O <sub>5</sub> /C ( % )
<b>NbO<sub>x</sub>@FP</b>	Nb <sub>2</sub> O <sub>5</sub> <sup>FP</sup>	Nb <sub>2</sub> O <sub>5</sub> C <sup>FP</sup> 800	Nb <sub>2</sub> O <sub>5</sub> C <sup>FP</sup> 900
	29.5 %	55,4%	54,3%
		53,1/46,7	54,3/45,6
<b>NbO<sub>x</sub>@BC</b>	Nb <sub>2</sub> O <sub>5</sub> <sup>BC</sup>	Nb <sub>2</sub> O <sub>5</sub> C <sup>BC</sup> 800	Nb <sub>2</sub> O <sub>5</sub> C <sup>BC</sup> 900
	19.5%	29,9%	27,1%
		65,2/34,8	72,0/28,0
<b>NbO<sub>x</sub>@MFC</b>	Nb <sub>2</sub> O <sub>5</sub> <sup>MFC</sup>	Nb <sub>2</sub> O <sub>5</sub> C <sup>MFC</sup> 800	Nb <sub>2</sub> O <sub>5</sub> C <sup>MFC</sup> 900
	35.0 %	48,3%	45,8%
		72,5/27,5	76,5/23,5

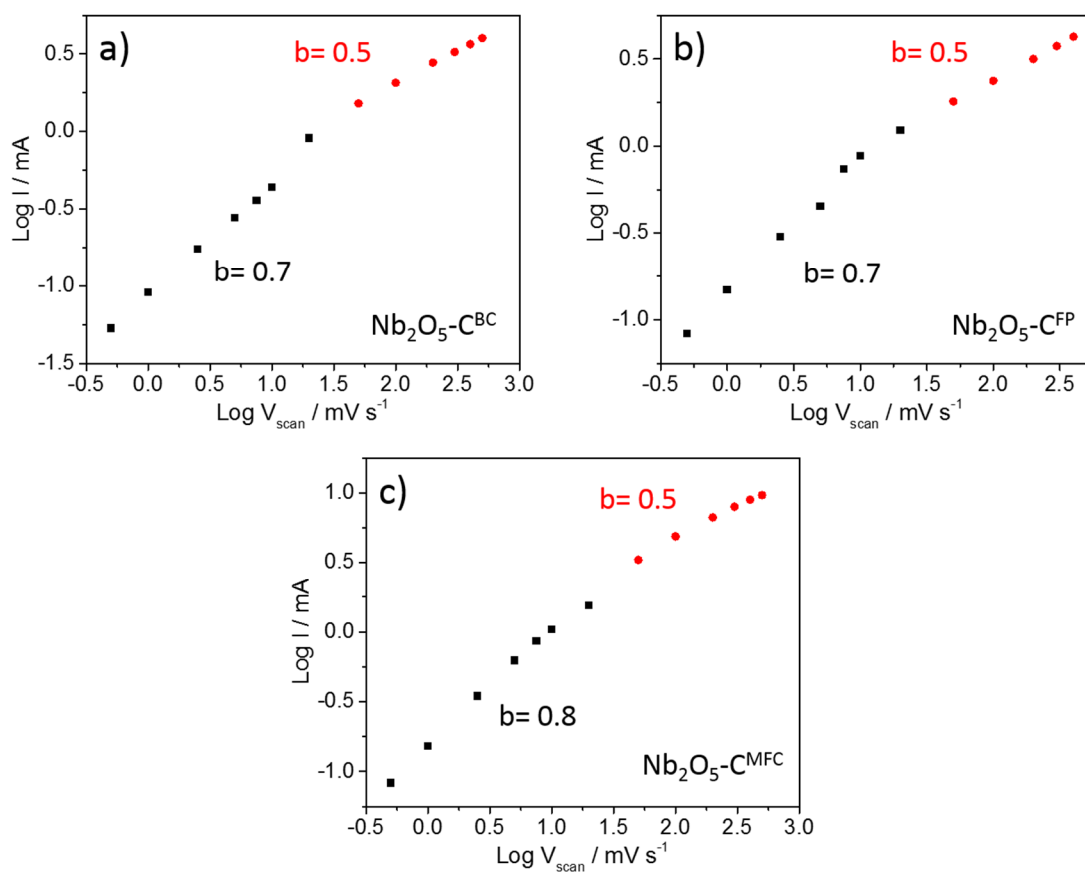
**Table 1:** Yields of TGA under air and argon of NbO<sub>x</sub>@FP, NbO<sub>x</sub>@BC and NbO<sub>x</sub>@MFC, name of the corresponding sample after thermal treatment and Nb<sub>2</sub>O<sub>5</sub>/C composition. a: under air by TGA analysis; b: under argon and determined by TGA analysis.

Samples	S <sub>BET</sub> <sup>a</sup>	S <sub>Micro</sub> <sup>b</sup>	S <sub>Meso</sub>	V <sub>p</sub> <sup>d</sup>	Ø <sup>e</sup>
NbO <sub>x</sub> @FP	48.9	4.2	44.7	0.18	99
NbO <sub>x</sub> @BC	49.3	3.9	45.4	0.19	101
NbO <sub>x</sub> @MFC	69.4	6.8	62.6	0.33	158
Nb <sub>2</sub> O <sub>5</sub> -C800 <sup>FP</sup>	192.6	49.5	143.1	0.36	65
Nb <sub>2</sub> O <sub>5</sub> -C800 <sup>BC</sup>	205.7	55.4	150.3	0.36	68
Nb <sub>2</sub> O <sub>5</sub> C800 <sup>MFC</sup>	372.3	258.5	113.8	0.39	75

**Table 2:** Summary of textural data obtained from N<sub>2</sub> porosimetry for sample before and after thermal treatment; <sup>a</sup>specific surface area (m<sup>2</sup> g<sup>-1</sup>), <sup>b</sup>Total surface of micropores (m<sup>2</sup> g<sup>-1</sup>) <sup>c</sup>Total surface of mesopores (m<sup>2</sup> g<sup>-1</sup>) <sup>d</sup>total pore volume (cm<sup>3</sup> g<sup>-1</sup>); <sup>e</sup>BJH average pore diameter calculated from the desorption branch (Å).

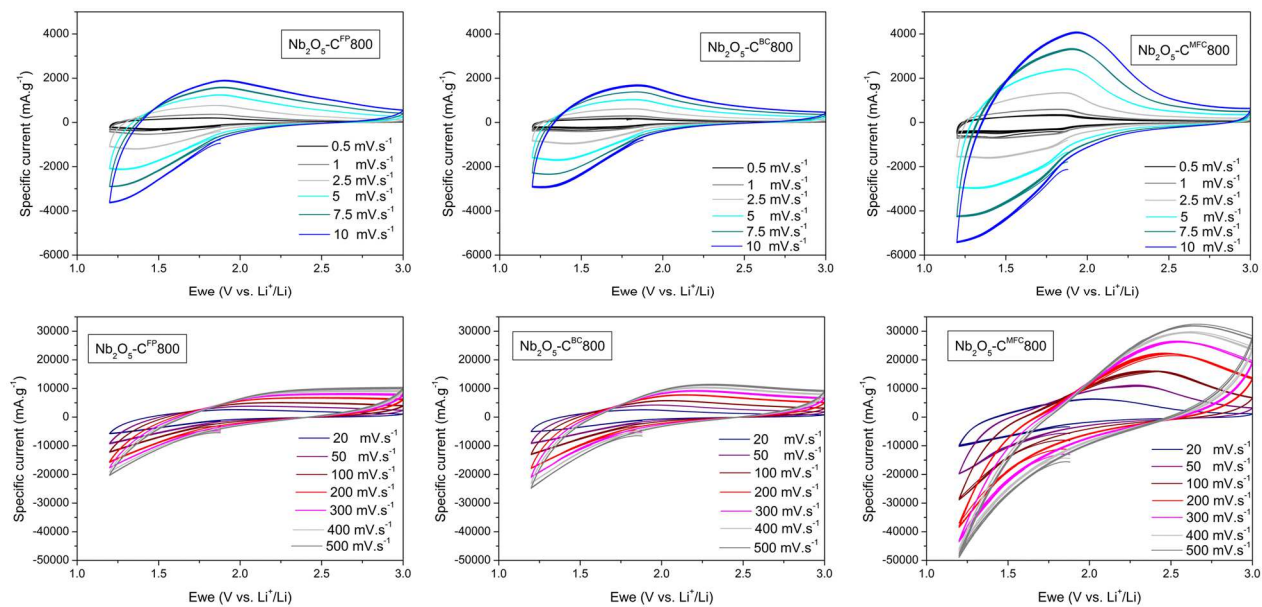


**Fig. 5:** a) Cyclic voltammograms of Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup> at low scan rates (from 0.5 to 10 mV s<sup>-1</sup>) and b) corresponding normalized CV ( $I v^{-0.5}$  - E) to analyze electrochemical mechanisms.

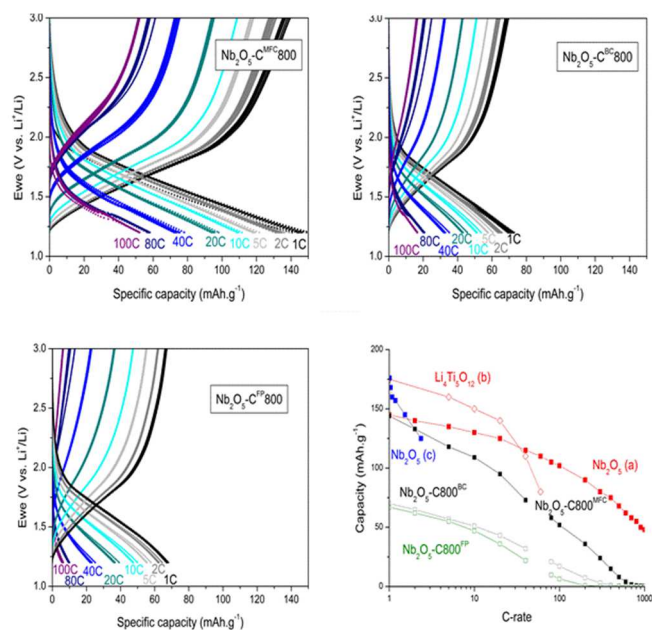


**Fig. 6:** Peak current analysis from CV of a) of  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}$ , a) of  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}$ , a) of  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}$

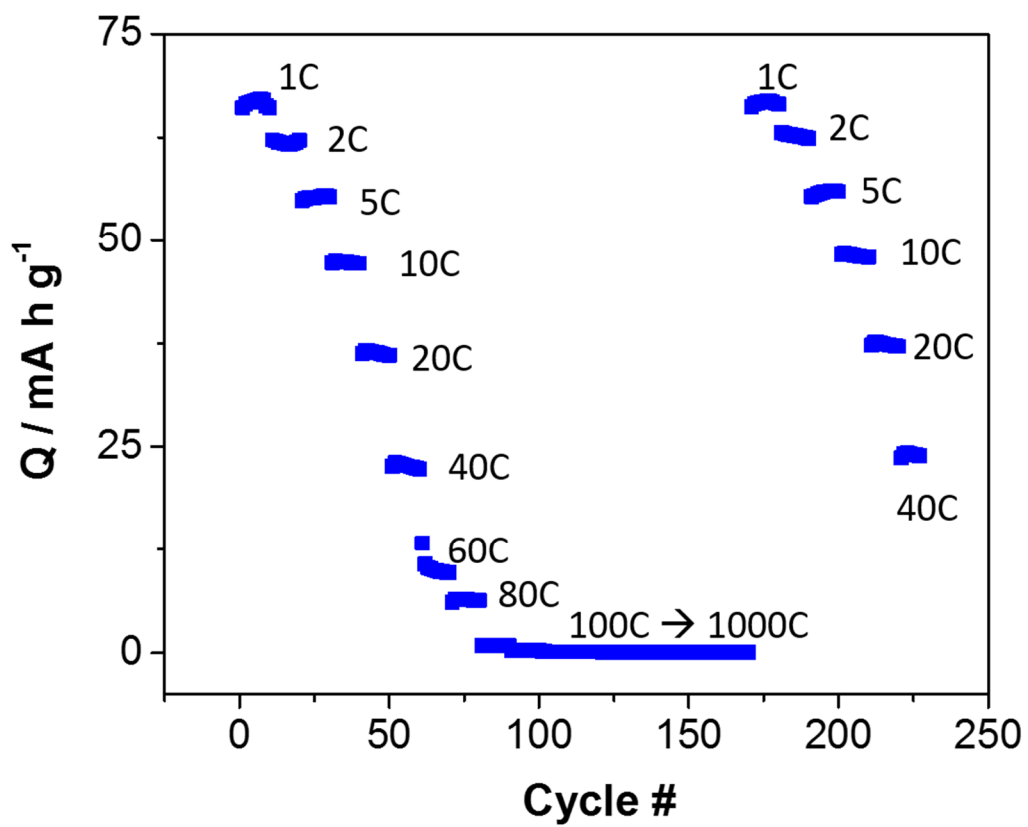




**Fig. 7:** Cyclic voltammograms of a,b)  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}800$ , c,d)  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}800$  and e,f)  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}800$ .



**Fig. 8:** C-rates of  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}800$ ,  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}800$  and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}800$ ; comparison of the rate capacity of  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}800$ ,  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}800$ ,  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}800$  with  $T\text{-Nb}_2\text{O}_5$ , at various C-rates.



**Fig. 9:** Capacity of Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>800 as a function of cycle number and varying the C-rate.

Starting sample	Name &	Name	Name
	Yield at 1000°C <sup>a</sup>	Yield at 800°C <sup>b</sup>	Yield at 900°C <sup>b</sup>
	Nb <sub>2</sub> O <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub> /C ( %)	Nb <sub>2</sub> O <sub>5</sub> /C ( %)
NbO <sub>x</sub> @FP	Nb <sub>2</sub> O <sub>5</sub> <sup>FP</sup>	Nb <sub>2</sub> O <sub>5</sub> C <sup>FP</sup> 800	Nb <sub>2</sub> O <sub>5</sub> C <sup>FP</sup> 900
	29.5 %	55,4%	54,3%
		53,1/46,7	54,3/45,6
NbO <sub>x</sub> @BC	Nb <sub>2</sub> O <sub>5</sub> <sup>BC</sup>	Nb <sub>2</sub> O <sub>5</sub> C <sup>BC</sup> 800	Nb <sub>2</sub> O <sub>5</sub> C <sup>BC</sup> 900
	19.5%	29,9%	27,1%
		65,2/34,8	72,0/28,0
NbO <sub>x</sub> @MFC	Nb <sub>2</sub> O <sub>5</sub> <sup>MFC</sup>	Nb <sub>2</sub> O <sub>5</sub> C <sup>MFC</sup> 800	Nb <sub>2</sub> O <sub>5</sub> C <sup>MFC</sup> 900
	35.0 %	48,3%	45,8%
		72,5/27,5	76,5/23,5

**Table 1:** Yields of TGA under air and argon of NbO<sub>x</sub>@FP, NbO<sub>x</sub>@BC and NbO<sub>x</sub>@MFC, name of the corresponding sample after thermal treatment and Nb<sub>2</sub>O<sub>5</sub>/C composition. a: under air by TGA analysis; b: under argon and determined by TGA analysis.

Samples	S <sub>BET</sub> <sup>a</sup>	S <sub>Micro</sub> <sup>b</sup>	S <sub>Meso</sub>	V <sub>p</sub> <sup>d</sup>	Ø <sup>e</sup>
NbO <sub>x</sub> @FP	48.9	4.2	44.7	0.18	99
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Nb <sub>2</sub> O <sub>5</sub> C800 <sup>MFC</sup>	372.3	258.5	113.8	0.39	75

**Table 2:** Summary of textural data obtained from N<sub>2</sub> porosimetry for sample before and after thermal treatment; <sup>a</sup>specific surface area (m<sup>2</sup> g<sup>-1</sup>), <sup>b</sup>Total surface of micropores (m<sup>2</sup> g<sup>-1</sup>) <sup>c</sup>Total surface of mesopores (m<sup>2</sup> g<sup>-1</sup>) <sup>d</sup>total pore volume (cm<sup>3</sup> g<sup>-1</sup>); <sup>e</sup>BJH average pore diameter calculated from the desorption branch (Å).