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REVIEW

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A Review on Pseudocapacitors: Advances in Nb Oxide - Sodium-Ion Systems

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Abstract: Pseudocapacitive supercapacitors have emerged as an important alternative to storage electrochemical energy. Among the several possible configurations of material for electrodes and electrolyte composition, the combination of oxides containing niobium and electrolytes based on sodium-ion has been presented as a very promising set. This review summarizes the main advances in the development of supercapacitors that use the Nb oxide - sodium-ion system. The electrochemical energy storage mechanisms are described and the influence of the type of electrolyte (aqueous or non-aqueous) is discussed. It was possible to verify that non-aqueous electrolytes are widely more used to assemble the Nb oxide - sodium-ion arrangements. For these systems the energy storage is controlled by the mechanism of intercalation/deintercalation of sodium-ions in the oxide structure. Despite non-aqueous electrolytes exhibit the advantage of operating in a wider window potential, they have disadvantages such as low electrical conductivity and sluggish Na^+ kinetics. To overcome these aspects, works in the field have generally focused on improving the properties of the oxides, especially concerning its conductivity through core@shell systems, composites or doping. On the other hand, few studies were found in the literature concerning the Nb oxide - sodium-ion systems that use aqueous electrolytes. Nevertheless, these works showed promising results such as an expansion of the potential window usually used in aqueous electrolytes or the possibility to apply the Nb oxide as cathode or anode.

Keywords: Energy storage; Supercapacitor; Niobium-based oxides; Sodium-ion supercapacitors; Pseudocapacitor

1. Introduction

Research and development in energy storage field represent a fundamental theme for sustainable technological progress towards decarbonization and mitigation of damage caused to the environment. This aspect is supported mainly by the following current technological needs: (a) to support renewable energy sources, as the supply of energy from some of these alternatives is not always available, such as solar and wind energy, part of this energy must be accumulated to compensate the alternation between supply and demand[1]; (b) to allow the progress and consolidation of the electrification of transportation[2,3]; (c) to enable the development and evolution of a whole new generation of portable electronic devices[4].

Currently, in terms of mobile and portable electrical energy storage, lithium-ion batteries are the well-established technology to meet these demands[4,5]. However, the technological dependency restricted to these devices can become an obstacle to the advancement of the technologies mentioned in the previous paragraph. Among the alternative devices to lithium-ion batteries that have been suggested, supercapacitors (also known as electrochemical capacitors) stand out for having a distinct set of characteristics such as: long life cycle, operational safety, high cyclability and fast recharge[6]. The electrochemical capacitors have an intermediate performance between conventional capacitors (characterized by a high power density) and batteries (characterized by a high energy density)[7], that is, they can store more energy per mass unit than conventional capacitors and can receive and donate charges faster than batteries. Today, most of the commercial electrochemical capacitors have electrodes composed of activated carbon, thus these devices store energy through the electrochemical double layer mechanism[7,8]. The energy stored by this mechanism is limited by the specific surface area of the active material, so the amount of energy (per unit mass or volume) capable of being stored in double layer capacitors is smaller than the lithium-ion batteries[9].

To overcome this limitation, the development of materials with pseudocapacitive properties, mainly transition metal oxides, has been suggested. These oxides can store energy from fast redox reactions that occur on the surface of the material and/or by intercalation and deintercalation of ions[10], which means that they can store a greater amount of energy than carbonaceous materials, without critical loss in device power density. In this context, niobium-based oxides are very promising candidates to be applied as active material for electrochemical capacitor electrodes, as these materials have favorable electrochemical properties, such as high chemical stability[11], several oxidation states such as +5 in Nb_2O_5, +4 in NbO_2, +3 in Nb_2O_3 and +2 in NbO[12], as well as the ability to allow the intercalation and deintercalation of ions[13]. These are notable characteristics, as they have a direct effect on the amount of energy that can be stored in an electrode made of this material.

In addition, another component that has a direct influence in the performance of a supercapacitor is the electrolyte, since the accumulation of energy occurs between the reactions that happen at the electrode/electrolyte interface. Regarding this, as an alternative to the use of lithium, sodium-ion based electrolytes have been suggested because they exhibit a similar storage energy mechanism to lithium-ion electrolytes[14]. Besides, sodium is an abundant element in the earth's crust, what can make electrolytes based on sodium-ion more affordable[15].

Therefore, this review presents the main works related to the use of niobium-containing materials for sodium-ion supercapacitors based on aqueous and non-aqueous electrolytes. Initially, some basic concepts concerning supercapacitors and pseudocapacitors are presented, such as: energy storage mechanisms, type of electrolyte (aqueous or non-aqueous) and role of sodium-ion when present in the electrolyte. Afterward, works that employ niobium-based oxides as electrodes in sodium-ion supercapacitors are described and discussed. Finally, the conclusions and perspectives on this research topic are presented.

2. Energy Storage Mechanisms in Supercapacitors

Double layer supercapacitors store electrical energy in an electrochemical double layer (Helmholtz layer) formed at the electrode/electrolyte interface. When the electrode is charged with a specific charge (positive or negative), opposing ionic charges within the electrolyte accumulate on the surface of the solid electrode. These charges from the electrolyte become adsorbed on the surface of the electrode and compensate the electronic charge on the surface of the active material, thus forming the so-called double-layer. The thickness of this layer depends on the size of the ions and the concentration of the electrolyte, typically ranging from 5 Å to 10 Å for concentrated electrolytes. The double layer storage mechanism is governed by an electrostatic process (non-faradaic), it means that charge transfer reactions do not occur[7].

Therefore, the basic operation of a double layer supercapacitor occurs in a manner where it promotes only an excess and a deficiency of electron charges at the negative and positive terminals during the charging process, which is reversed during the discharging process (**Figure 1**). Through the external circuit, only electrons need to be moved to and from the electrode surfaces, while the cations and anions of the electrolyte are transported within the solution to the charged interfaces. Since the charging and discharging of these double-layer devices take place without any chemical, phase, or compositional changes involved, the processes are highly reversible, what makes the double layer supercapacitor a device with a high level of cyclability[16].

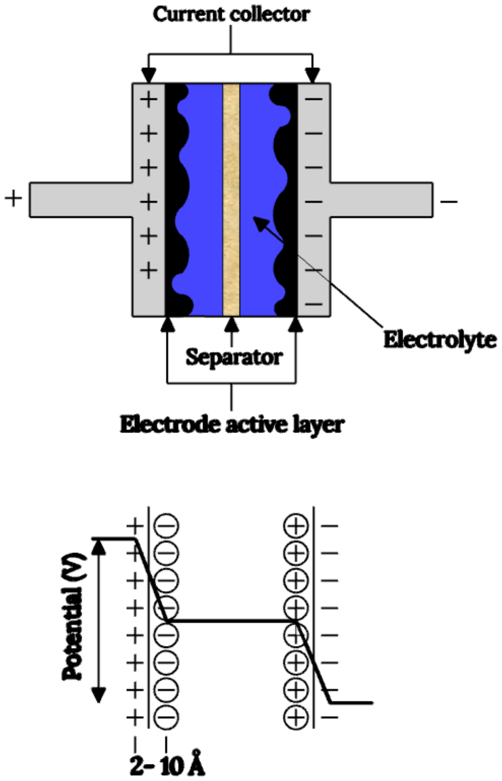

Figure 1. Representation of an electric double layer capacitor (EDLC)

It is crucial to distinguish between energy storage processes based on faradaic and non-faradaic mechanisms. In non-faradaic processes, charge storage occurs electrostatically by accumulating opposite charges (positive and negative) at two interfaces separated by a vacuum or a molecular dielectric (such as in double layer supercapacitors). On the other hand, faradaic processes involve charge storage through electron transfer, which leads to chemical or oxidation state changes in electroactive materials following Faraday's laws related to the electrode potential. This mechanism is observed in battery storage processes. However, in certain cases of double-layer charging, there is a partial electron transfer that occurs at a significant rate, resulting in a mechanism known as “pseudocapacitance”. In the pseudocapacitive mechanism, faradaic charge transfer takes place through the double layer via electron transfer between the electrolyte and the electrode. This charge originates from a desolvated ion that becomes adsorbed on the electrode surface. However, the adsorbed ion does not undergo a chemical reaction with the electrode atoms. Instead, there is a transfer of electronic charge as a result of a rapid sequence of reversible processes involving oxidation-reduction, electrosorption, or ion intercalation on the surface of the supercapacitor electrode[16].

The concept of pseudocapacitance was initially proposed by Conway and Gileadi in 1962[17]. The authors introduced the term to describe the reversible capacitance associated with the electrochemical adsorption of ions onto the electrode surface. In their study, they proposed a kinetic theory that suggested a linear correlation between the heat of adsorption and the surface coverage of the electro-deposited species. This theory led to the development of a capacitance definition based on surface coverage[18]. Later, Conway further developed the concept of pseudocapacitance and categorized it into three primary mechanisms: adsorption pseudocapacitance (also known as underpotential deposition), redox pseudocapacitance, and intercalation pseudocapacitance (**Figure 2**)[16].

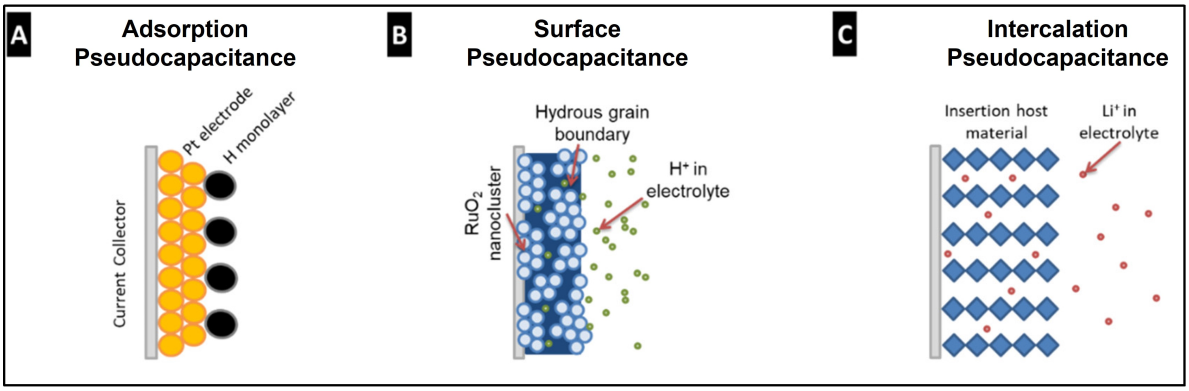

Figure 2. Illustration of the three pseudocapacitance mechanisms: (a) Adsorption pseudocapacitance; (b) redox pseudocapacitance; (c) intercalation pseudocapacitance. Adapted with permission from ref. [18]. Copyright 2020 American Chemical Society

Capacitance attributed to the adsorption mechanism takes place when metal ions create an adsorbed monolayer on the surface of a distinct metal that exceeds their redox potential. A well-known example of adsorption pseudocapacitance is the underpotential deposition of lead (Pb) onto a gold electrode (Au)[19]. This process involves the underpotential deposition of Pb^{2+} at a particular potential on the surface of an Au electrode, resulting in a significant enhancement of capacitance[20,21].

Redox pseudocapacitance or surface redox pseudocapacitance primarily occurs when electrolyte ions are electrochemically adsorbed onto the active material surface or subsurface of the electrode, involving faradaic charge transfer[19]. This phenomenon was initially observed in ruthenium dioxide, where redox processes were detected by cyclic voltammetry, exhibiting the oxidation states of 2^+, 3^+, and 4^+ in RuO_2. This simultaneous process, coupled with proton transfer, gives rise to redox pseudocapacitance, which serves as the dominant charging mechanism for this material[20]. Here we will refer to this mechanism as “surface pseudocapacitance”.

Due to the development of advanced nanostructured materials, particularly transition metal oxides, a third type of pseudocapacitance has been recently observed. Known as intercalation pseudocapacitance, this phenomenon occurs when electrolyte ions intercalate into the tunnels or layers of a redox-active material within the electrode. This intercalation process involves faradaic charge transfer without causing any changes in the crystallographic phase of the material[19]. The absence of a phase transition is what distinguishes electrodes that exhibit intercalation pseudocapacitance from those that exhibit battery-like intercalation.

In surface pseudocapacitance, charge transfer takes place only on the surface of the electrode, without the electrolyte ions inserting themselves into the structure of the electrode material. Conversely, in intercalation pseudocapacitance the ions are inserted into the tunnels or in positions of vacancy inside the structure of the electrode material. These intercalated ions participate in rapid surface redox processes with the adjacent material. Unlike surface pseudocapacitance, the pseudocapacitive intercalation phenomenon extends beyond the surface, occurring within the bulk of the active material. Consequently, the presence of the intercalation mechanism is expected to result in an increased energy density in pseudocapacitive processes. Several cations, including Li^{+}[19,22], Na^{+}[23,24], K^{+}[25,26] among others, exhibit electrochemical intercalation effect in a pseudocapacitive process. In fact, some of these ion intercalation processes have been found to generate pseudocapacitive effects that promoted capacitances greater than those achieved by double-layer porous carbons[20] Recently studies have also reported pseudocapacitance by anion intercalation, induced by oxygen ions intercalated in the structure of the electrode material[20,27,28].

In a recent review organized by Liu *et al.*[20], the authors summarized the significant advancements in electrode and electrolyte materials to the intercalation pseudocapacitive mechanism. According to the authors, a key requirement responsible for facilitating the intercalation pseudocapacitance process is that the electrode material must have a crystalline structure with two-dimensional channels. These channels enable rapid ion diffusion, contributing to the overall performance of the pseudocapacitor. Furthermore, the material must exhibit sufficient stability to prevent any structural phase transition during ion intercalation. Perovskite oxides, T-Nb_2O_5 and TiO_2-B are the most explored materials for typical intercalation pseudocapacitive electrodes due to their electrochemical behaviour, even in their bulk form. In contrast, there are other materials that only exhibit intercalation pseudocapacitive behaviour when synthesized as nanoparticles. This effect can be attributed to the fact that in nanostructured materials, the ion diffusion distance is reduced, and the redox reaction without phase transformation reduces the energy barrier, which makes the electrochemical reaction on this type of electrode kinetically favored[20].

Differentiating between surface redox pseudocapacitance and intercalation pseudocapacitance only based on the shape of cyclic voltammetry (CV) and galvanostatic charge/discharge curves can be challenging due to the presence of faradaic charge transfer in both processes. However, it is known that intercalation pseudocapacitance involves the volume of the active material and is not limited by the specific surface area of the electrode like surface redox pseudocapacitance. As a result, processes where intercalation pseudocapacitance is present are expected to exhibit higher capacitance values. It should be noted that in practical applications, the total charge stored in a supercapacitor can involve a combination of processes, including the faradaic process associated with the insertion of cations/anions (intercalation pseudocapacitance), the faradaic process associated with adsorption and surface atom transfer (surface pseudocapacitance), as well as the non-faradaic contribution from the double-layer effect. Therefore, a comprehensive understanding of the various mechanisms involved in the electrochemical energy storage is essential to evaluating and optimizing the performance of a supercapacitor[16,19,20].

Since pseudocapacitive materials take advantage of redox effects, it's important to distinguish which materials exhibit suitable behavior for pseudocapacitors and which materials are better suited for batteries. Sampaio *et al.*[29] investigated the kinetic performance of Nb oxide nanotubes using electrochemical characterization data. As described by the authors, a mathematical methodology for analyzing sweep voltammetry data can be employed to differentiate pseudocapacitive materials from battery-like ones. The kinetic analysis method involves examining cyclic voltammetry data at different scan rates, using a power law relationship between current density (j) and scan rate (v). The value of "b" represents the slope of the log (j) *vs*. Log (i) curve. When these values are approximately 1, the primary current response is capacitive (indicative of pseudocapacitive material). When the value of "b" is close to 0.5, the charge storage mechanism is predominantly dominated by diffusion-controlled processes (battery-like materials).

$$j = av^{b}$$

This investigative approach to studying the kinetics of charge storage mechanisms to distinguish between capacitive and diffusion-controlled processes has provided valuable insights into these materials. Such research have demonstrated that conventional battery-like materials can have their characteristics altered through nano/microstructural design: the energy storage mechanism at the nanoscale to shift towards capacitive dominance. Wang *et al.*[30] showed that by enhancing the nano/microstructural design of the material, behavior previously dominated by diffusion-controlled processes can transition to a capacitive one.

This effect can be attributed to the rapid diffusion of electrolyte ions and mass transfer reactions facilitated by the material's structure. Furthermore, the authors also found that the asymmetric design of the device can benefit the capacitive mechanism. The study illustrates that the transformation of conventional battery-like materials into new ones dominated by capacitance is achievable through nano/microstructural design and asymmetric capacitance balancing.

In this context, investment in the development of nanoscale materials has proven to be highly promising, given that nanostructured pseudocapacitive materials in various morphologies can enable ion intercalation within the structure and facilitate shorter ion diffusion pathways in the electrolyte. This, in turn, allows for rapid redox reactions, contributing to achieving exceptionally high specific capacitances.

2.1 The role of Electrode Materials

The electrode is the most important component in the performance of an electrochemical capacitor, usually consisting of current collector, active material, conductive additive and binder.

The current collector has the function of supporting the active material and connecting the electrode to the outer junction of the electrochemical capacitor. This component usually has a thickness between 15 μm and 40 μm. The main factors that influence the choice of current collector material are cost, density, processability and mainly, chemical stability with the electrolyte. The main materials used are aluminum (for organic electrolytes), nickel or stainless steel (aqueous electrolytes of strong bases or acids)[9].

The active material generally does not have high electrical conductivity, so, it is necessary to add some conductive material in the form of particles to the electrode in order to reduce the equivalent serial resistance. The main material used for this purpose is carbon black[31].

The binder is necessary to keep the various components of the electrode together, that is, it must generate great cohesion between the particles of the binder itself, the active material and the conductive additive, in addition to providing adhesion between these particles and the current collector. The amount of binder to be added to the mixture with the other particles must be low to avoid an increase in the equivalent serial resistance and a decrease in gravimetric capacitance. The main types of binder are: polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyvinyl acetate (PVA) and carboxymethylcellulose (CMC), the first two are the most used in electrochemical capacitors[9].

The active material is the direct responsible for storing the electrical energy at the electrode. This component together with the electrolyte define the energy storage mechanism of the device. Carbon-based materials are by far the most used material in electrochemical capacitors due to a peculiar combination of properties, such as: large surface area (usually, up to 2000 m^2/g); good corrosion resistance; high temperature stability; control of pore structure; processability; compatibility with other materials and relative low cost[31]. They can be found in several forms, such as: activated carbon, carbon derived from carbides, carbon in zeolite structure, carbon aerogel, carbon nanotubes and graphene[32]. From those, activated carbon is currently the most widely used in commercial electrochemical capacitors. This type of active material stores the energy electrostatically by the formation of the electrochemical double layer (non-faradaic processes).

Another type of material that has been applied as active material in electrochemical capacitors are the transition metal oxides and, compared to carbon-based materials, they present higher specific capacitance and higher energy density[33]. Ruthenium oxide (RuO_2), cobalt oxide (Co_3O_4), vanadium oxide (V_2O_5), manganese oxide (MnO_2) and nickel oxide (NiO) can be pointed out as the main examples of oxides used for this application[34]. Electrodes made of transition metal oxides have their energy storage mechanism governed by pseudocapacitance, as mentioned earlier.

2.2 The Role of Electrolyte

A supercapacitor's electrolyte has the function of providing the ions that will counterbalance the charge of the electrodes, thus forming the electrical double layer or promoting redox and/or intercalation processes. According to equation 1 and equation 2, the energy (E) and the power (P) of a supercapacitor are significantly influenced by the electrolyte, as this component is directly responsible for characteristics such as operational voltage (V) and equivalent serial resistance (R_S). Besides, the electrolyte has important impact on the capacitance (C) of the system[35,36].

$$E = \frac{1}{2}CV^2 \quad (1)$$

$$P = \frac{V^2}{4R_S} \quad (2)$$

There are two main types of electrolytes for supercapacitors: aqueous and organic (non-aqueous). **Table 1** exhibits the main advantages and disadvantages of each one.

Table 1. Advantages and disadvantages of aqueous and non-aqueous electrolytes for supercapacitors[37-39]

Type of electrolyte	Advantage	Disadvantage
Aqueous	Low cost High ionic conductivity Environmentally friendly High capacitance Non-inflammability Non-toxicity High manipulability	Limited working temperature Limited potential window (1.23 V)
Non-aqueous (organic)	High potential window Wide working temperature Commercial maturity	High internal resistance High volatility Inflammability Toxicity Low thermal stability High production costs

Aqueous electrolytes are made from water with the addition of some ionic compound. They can be divided into three main groups: acid electrolytes (for example H_2SO_4), basic electrolytes (for example KOH) and neutral electrolytes (for example Na_2SO_4)[40]. Aqueous electrolytes are characterized by having low cost, high ionic conductivity, and higher capacitance values[37] when compared to organic electrolytes. However, they have an operational voltage of the electrochemical cell of approximately 1 V, due to the decomposition of water that occurs around 1.23 V (evolution of hydrogen or oxygen)[40]. Besides, current energy storage systems that use aqueous electrolyte, such as lead-acid and nickel-cadmium batteries, contain harmful heavy metals in their constitution[41], which makes them potentially harmful to the environment.

Organic electrolytes (non-aqueous) are mainly composed of organic solvents, such as acetonitrile and propylene carbonate. Salts based on tetraethylammonium and tetrafluoroborate (as examples) are dissolved in these solvents. The main attribute of this type of electrolyte is the operating voltage of the cell, usually between 2.5 V and 2.8 V[40]. When compared to aqueous electrolytes, organic electrolytes have relatively low electrical conductivity, which leads to a lower power density, lower specific capacitance, higher cost and operational safety issues, such as flammability, volatility and toxicity[40]. In addition, devices that use this type of electrolyte have a higher cost, since the assembly process is complex due to the need to avoid electrolyte contaminants (for example, water)[42].

2.3 The Role of Sodium-ion

As previously mentioned, pseudocapacitive behaviour has been observed in various cations, with Li^+ as the most popular intercalation charge carrier in the literature. In addition, ions such as K^+, Mg^{2+}, and Al^{3+} have also been reported as capable of promoting the pseudocapacitive intercalation mechanism[20,43]. Sodium has been considered as a good alternative for lithium, because it overcomes the cost and supply issues and has a similar working chemistry[44,45].

Sodium-ion Na^+ as electrolyte charge transporter in supercapacitors has gained significant attention over the last years and the first relevant work in the field was presented by Chen *et al.*[46]. The authors developed a composite made by V_2O_5 nanowires and carbon nanotubes and applied this material as anode with activated carbon as cathode to assemble an asymmetric sodium-ion capacitor (SIC). The proposed device was able to achieve results comparable to lithium-ion system.

However, sodium has a larger ionic radius (1.02

Å) and higher ionic mass (22.99 g/mol) compared to lithium (0.76 Å and 6.94 g/mol, respectively)[47], consequently slower kinetics are expected. Therefore, the use of sodium-ion electrolyte demands electrodes with a reasonable interplanar spacing, considering capacitors with intercalation pseudocapacitance.

Many materials have being studied as electrodes for supercapacitors based on Na-ion electrolyte. A few examples are carbon-based[48-50], sulphides[51-53], Ti based oxides[54-56], organic materials[57,58], and Nb based oxides. A schematic summarization of emerging materials that are typically used as cathode or anode is shown in **Figure 3**.

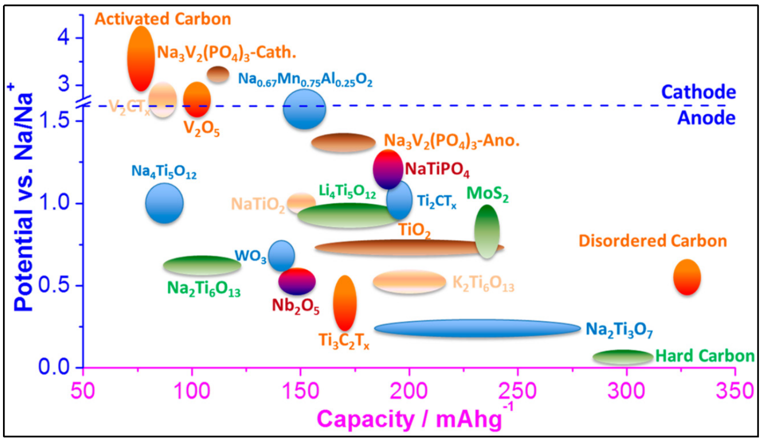

Figure 3. Plot of the theoretical capacity and operation potential of promising electrode materials for SICs. Reproduced with permission from ref. [59]. Copyright 2018, American Chemical Society

3. Niobium Based Materials Applied to Sodium-ion Supercapacitors

Electrodes made from niobium-based oxides are promising candidates for supercapacitors because they present electrochemical properties that qualify them as a bifunctional material, that is, they can be applied as both cathode and anode. There is at least 10 years of research on niobium-based materials applied to sodium-ion supercapacitors. **Table 2** summarizes the findings of researchers over the years.

Table 2. Summary of works and main results of niobium-based materials for sodium-ion supercapacitors*

Authors	Ref.	Year	Synthesized material	Synthesis method	Electrolyte	Max. Stable Capacity (*vs.* Na/Na^+)	Max. Capacitance	Potential window (V)	Max. Energy density	Max. Power density
Kim *et al.*	[36]	2012	T, TT and amorphous Nb_2O_5	Aqueous sol-gel for amorphous and T, non-aqueous for TT	1 M $NaClO_4$ in propylene carbonate (PC)	40 C/g at 5 mV/s (amorphous phase)	20 μF/cm^2 Half-cell with Na as counter and reference electrode	1.2-3 Same half-cell	Not informed	Not informed
Lim *et al.*	[60]	2016	T-Nb_2O_5 nanoparticles combined with reduced graphene oxide (rGO)	Method based on a water-in-oil microemulsion system and a charge matching assembly	1 M $NaPF_6$ in 1:1 volume/volume ethylene carbonate (EC)/dimethyl carbonate (DMC) + 5 wt% fluoroethylene carbonate (FEC)	110 mAh/g at 3 A/g	Not informed	0.01-3 Full-cell	76 W • h/kg at 80 W/kg	20,800 W/kg at 6 W • h/kg
Li *et al.*	[61]	2016	Nb_2O_5 nanosheets and peanut shell carbon (PSC)	Hydrothermal synthesis, followed by (for PSC) grounding and calcination	1 M $NaClO_4$ in 1:1 v/v EC/PC + 5 wt% FEC)	200 mAh/g at 0.05 A/g after 500 cycles	Not informed	1-3 Full-cell	43.2 W • h/kg at 160 W/kg	5760 W/kg at 24 W • h/kg

Continuation Table:

Authors	Ref.	Year	Synthesized material	Synthesis method	Electrolyte	Max. Stable Capacity (*vs*. Na/Na^+)	Max. Capacitance	Potential window (V)	Max. Energy density	Max. Power density
Tong *et al.*	[62]	2018	Sandwich-like mesoporous Nb_2O_5/graphene/mesoporous Nb_2O_5 (G@mNb_2O_5) nanosheets	Hummer's method followed by two-step hydrolysis synthesis	1 M $NaClO_4$ in 1:1 v/v EC/PC + 5 wt% FEC	125 mAH/g at 2 A/g after 2000 cycles	34 F/g at 0.05 A/g Full-cell	0.01-2.5 Full-cell	56.1 W • h/kg at 120 W/kg	7200 W/kg at 9.7 W • h/kg
Wu *et al.*	[63]	2018	Mesoporous m-Nb_2O_5/C composite	Hydrolysis synthesis followed by drying and annealing	1 M $NaClO_4$ in 1:1 v/v EC/PC + 0.5 wt% FEC	125 mAH/g at 1 A/g after 1000 cycles	Not informed	1-4 Full-cell	73 W • h/kg at 250 W/kg	20 kW/kg at 16.8 W/kg
Wang *et al.*	[64]	2018	Nb_2O_5 nanowires encapsulated in graphene	Hydrothermal synthesis for Nb_2O_5; plasma-enhanced chemical vapor deposition (PECVD) for composite	1 M $NaClO_4$ in 1:1 v/v EC/DMC + 5 wt% FEC	130 mAH/g at 20 C after 1000 cycles	Not informed	1-4.3 Full-cell	113 W • h/kg at 80 W/kg	5330 W/kg at 62 W • h/kg
Li *et al.*	[65]	2019	m-Nb_2O_5 Carbon Nanofiber (CNF) and graphene framework (GF)/mCNF	Electrospinning followed by annealing and SiO_2 etching	1 M $NaPF_6$ 1:1 v/v EC/DMC + 5 wt% FEC	248.6 mAh/g at 0.5 C after 500 cycles	Not informed	0-4 Full-cell	124 W • h/kg at 200 W/kg	60 kW/kg at 55 W • h/kg
Wu *et al.*	[66]	2019	Orthorhombic niobium oxyfluoride/carbon nanobelts (T-Nb_2O_5-xFy $\subset$C-NBs)	Ethanol-assisted solvothermal synthesis	1 M $NaClO_4$ 1:1 v/v EC/PC + 0.5 wt% FEC	165 mAh/g at 1 A/g after 10000 cycles	~40 F/g at 1 A/g Full-cell	1-4 Full-cell	86.8 W • h/kg at 250 W/kg	18 kW/kg at 32.1 W • h/kg
Jia *et al.*	[67]	2020	Nb_2O_5 nanotubes and nanowire-to-nanotube homo-junctions grown on carbon cloth (CC)	Hydrothermal synthesis	1.5 M $NaClO_4$ in 1:1 v/v EC/DMC + 5 wt% FEC)	125 mAh/g at 1 A/g after 1000 cycles	38.8 F/g at 0.03 A/g Full-cell	0-4 Full-cell	195 W • h/kg at 120 W/kg	7328 W/kg at 28 W • h/kg
She *et al.*	[68]	2020	Sulfur-doped Nb_2O_5 within N and S co-doped microporous carbon nanofiber (S-Nb_2O_5@NS-PCNF)	Electrospinning followed by a sulfidation treatment	1 M $NaClO_4$ in 1:1 v/v EC/DMC + 5 wt% FEC)	173 mAh/g at 2 A/g after 10000 cycles	Not informed	1-4.3 Full-cell	112 W • h/kg at 80 W/kg	7949 W/kg at 55 W • h/kg

Continuation Table:

Authors	Ref.	Year	Synthesized material	Synthesis method	Electrolyte	Max. Stable Capacity (*vs*. Na/Na^+)	Max. Capacitance	Potential window (V)	Max. Energy density	Max. Power density
Real *et al.*	[69]	2020	Niobium pentoxide (Nb_2O_5) decorated multiwalled carbon nanotube (MWCNT)	Mixing of MWCNT solution and Nb_2O_5 powder followed by heat treatment	1 M $NaClO_4$ in 1:1 v/v EC:DMC	68 mAh/g at 0.025 A/g after 100 cycles	192 F/g Full-cell	0-3 Full-cell	5.4 W•h/kg at 98.7 W/kg	24.671 kW/kg at 2.7 W•h/kg
Idrees *et al.*	[70]	2016	3D-hollow hierarchical Nb_2O_5 superstructures	Hydrothermal synthesis	1 M Na_2SO_4 (aqueous)	Not informed	366 F/g at 1 A/g Half-cell with Pt counter-electrode	0-1.2 Same half-cell	86 W • h/kg at 650 W/kg	6500 W/kg at 58 W • h/kg
Upadhyay *et al.*	[12]	2018	Vertically aligned Nb_2O_5 nanochannel layers	Self-organizing electrochemical anodization in molten electrolyte	1 M Na_2SO_4 (aqueous)	Not informed	100 mF/cm^2 at 0.001 A/cm^2 Half-cell with Pt counter-electrode	(-0.2)-(-1.3) Same half-cell	Not informed	Not informed
Santos *et al.*	[71]	2022	$Na_2Nb_2O_6$ • H_2O, $Na_2Nb_2O_6$, $NaNbO_3$; $(H_3O)_2Nb_2O_6$ and $(H_3O)_2Nb_2O_6$ • H_2O nanowires	Hydrothermal synthesis, followed by different heat treatments and protonic exchange	1 M Na_2SO_4 (aqueous)	Not informed	Not informed	0-(-1.3)~(-1.7) Half-cell with Pt counter-electrode	Not informed	Not informed
Sampaio *et al.*	[29]	2022	Highly ordered nanotubular niobium oxide	Potentiostatic anodization	1 M Na_2SO_4 (aqueous)	Not informed	20 mF/cm^2 at 1 mA/cm^2 Half-cell with Pt counter-electrode	(-0.2)-(-1.2) Same half-cell	Not informed	Not informed

* The mentioned full-cells consisted of a niobium based material for the anode and a carbon based material, generally activated carbon (AC), for the cathode.

The studies published in this area largely focused on niobium pentoxide (Nb_2O_5), due to its characteristic of working in higher potentials, as well as its intercalation mechanism when used as anode, which is superior than alloy and conversion types of anodes because of its low volume expansion, fast charge-discharge ability, and superior cycling stability[72]. However, the materials are limited by their poor electric conductivity (for Nb_2O_5 it is 3×10^{-6} S/cm[73]) and, even though their theoretical capacity is higher than that of other oxides (approximately 200 mA • h/g for Nb_2O_5[74]) and can be applied in higher potentials, it is still lower than for other electrode materials (such as $Li_4Ti_5O_{12}$[75] and TiO_2[76]).

For a better understanding of the intercalation mechanism of ions into the structure of orthorhombic Nb_2O_5, **Figure 4** illustrates how lithium ions are transported through the Nb_2O_5 interplanar spacings. This scheme provides a visualization on how sodium ions can intercalate into niobium based electrodes, considering the spacing of approximately 4 Å in the (001) plane[77] and the sodium ionic radius of 1.02 Å. Besides intercalation, when electrodes made of Nb_2O_5 are tested, the importance of Nb^{5+}/Nb^{4+} (at 1.5~1.8 V) and Nb^{4+}/Nb^{3+} (below 1.5 V) redox pairs[78] is usually pointed out.

Many studies are focused on increasing the surface area by developing nanostructured materials and/or improving electron conductivity via insertion of conductive materials on the matrix or doping. Besides, most of the works use as electrolyte 1 M $NaClO_4$ or $NaPF_6$ in different organic solutions, such as propylene carbonate (PC), ethylene carbonate (EC)/dimethyl carbonate (DMC) or PC in 1:1 ratio in volume with the addition of 5 wt% or 0.5 wt% of fluoroethylene carbonate (FEC), *etc*.

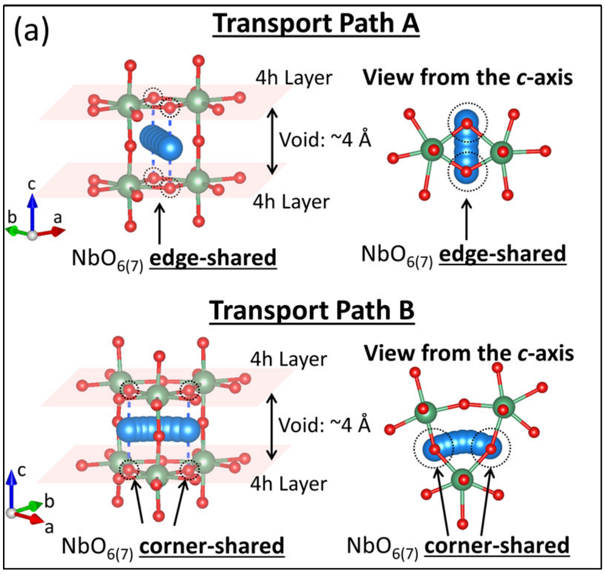

Figure 4. Two Li-ion transport path topologies (path A and path B) for Li-ion migration from one bridge site to another. The bridging coordination between Li ions and O_{4h} is marked with blue dashed lines, and the bridged O_{4h} are marked with black dashed circles for clarity. Reproduced with permission from ref. [77]. Copyright 2017, American Chemical Society

In order to characterize the electrochemical properties of a proposed electrode, authors usually develop a half-cell with metallic Na as counter and reference electrode. This kind of experiment, which resembles a battery device, is generally the focus of studies on applications of niobium-based electrodes for sodium ion batteries (SIBs). Those studies that only mention half-cells will not be the focus of this review, but some will be mentioned here for contributing with the understanding of niobium-based electrodes applied to SICs. Moreover, many experiments prepare a slurry containing up to 10 wt% of an insulating binder and up to 15 wt% of a conductive additive for preparation of electrodes for half and full-cells; this is done because of the powder macrostructure of the prepared materials, although there have been materials that are developed as films, not needing this process. The cells are generally made as a CR2032-type coin cell, which avoids contamination of the electrolyte by air and can be used as an actual energy storage device. It is worth emphasizing that full-cells are usually hybrid supercapacitors, with the niobium oxide electrodes as a pseudocapacitor and the other electrode (carbon-based material) as an electric double-layer electrode.

One of the first studies on the applications of niobium-based materials to Na-ion energy storage was made by Kim *et al.*[36]. In this study, Nb_2O_5 nanofilms were used as working electrode in a three-electrode cell, in $LiClO_4$ and $NaClO_4$ solutions, with the purpose of investigating the effects of different solid phases on its electrochemical properties, comparing the orthorhombic (T), monoclinic (TT) and amorphous phases[79]. The authors conclude, through the clear difference in capacitance for each phase of Nb_2O_5, that Li^+ insertion occurs and causes fast faradaic reactions (therefore, the electrodes were acting as a pseudocapacitor electrode), but they also conclude that the capacitance difference is non-existent when Na^+ ions are used in solution, implying that it must be because of the ion's size, which hinders insertion, having only double layer capacitance as result. Despite being more of a battery-like system, this study is interesting for putting into question the use of Na^+ ion electrolyte with Nb based electrodes. Future studies, however, would seriously move away from the disbelief that sodium ion insertion does not happen.

In 2016[60], there was already promising research with the study of a Na-hybrid supercapacitor (Na-

HSC) with core-shell Nb_2O_5@C nanoparticles (NPs) combined with reduced graphene oxide (rGO) as anode and activated carbon (AC) as cathode, utilizing $NaPF_6$ as electrolyte. The material achieved power density of 20,800 W/kg (with 6 W • h/kg) at 8 A/g and energy density of 76 W • h/g (with 80 W/kg) at 0.03 A/g, maintaining good cycling stability after 3000 cycles at 1 A. The system also managed to reach 110 mA • h/g at 3 A/g and ≈ 285 mA • h/g at 0.025 A/g *vs*. Na/Na^+ half-cell tests (0.01-3.0 V), already surpassing the theoretical capacity of pure Nb_2O_5. For a brief comparison, in a similar study of 2014[80], which utilized the same material but with $LiPF_6$ electrolyte, the maximum power density was 16,528 W/kg (with 5 W • h/kg) and energy density of 63 W • h/kg as well as a reversible capacity of 180 mA • h/g at 0.05 A/g. In other words, the Na-ion study surpassed the lithium-ion results, although no clear hypothesis for the reasons for this was proposed.

One of the most sophisticated energy storage mechanisms proposed for a Na-ion Nb-based HSC was done[81] investigating a mesoporous Nb_2O_5/carbon composite in a half-cell, by experimenting with *ex situ* XRD and XPS analysis, arrived at the following conclusions for the Na storage mechanism: during discharge above 0.3 V Na ions are inserted in Nb_2O_5 via surface reactions; below 0.3 V, the $Na_\delta Nb_2O_5$ that was formed partially and irreversibly transforms into NbO and Na_2O, whilst amorphization occurs; Na ions are then stored in the amorphous $Na_{1.34}Nb_2O_5$ phase, and charging the system will cause deintercalation to occur, forming $Na_{0.28}Nb_2O_5$. It's important to note that with the many different materials that are developed for this application, there is no way to propose one universal mechanism that explains the step-by-step energy storage process of niobium-based electrodes (there are good examples of other studies of energy storage mechanisms in similar systems[61,82]); this is one of the tasks for each of the studies published on the field.

In the development of composite materials, a study of the physical-chemical relations between the materials is important for a good understanding of the system. A core@shell mesoporous Nb_2O_5@carbon NPs used as anode in a hybrid supercapacitor[63] was developed, and the authors identified between the niobium pentoxide core and the graphite shell an intermediary layer made of chemically bonded NbC, to which they attributed significant electrical conductivity improvement, for instance. The system achieved an energy density of 72.9 W • h/kg (with 250 W/kg) at 0.1 A/g and a power density of 20,000 W/kg (with 16.8 W • h/kg), resulting in an improvement in relation to the previously 2016 discussed work[60], given that it maintained a better balance between increase in power/energy and decrease of the correlated property, as well as a higher capacity of 252 mA • h/g at 0.05 A/g.

Considerations of possible limitations of the developed composites can also be made, such as in a study that, assuming that the graphene matrices utilized in previous works could hinder the transport of Na^+ ions to the surface of Nb_2O_5, investigated the use of Nb_2O_5 nanowires (NWs) encapsulated under ultrathin graphene shells as anode, with the graphene shells having controllable surface defects to allow Na^+ transport[64]. Furthermore, the authors tested a bendable device made with the same system of electrodes and electrolyte and found out that bending the energy storage device showed stable electrochemical performances, suggesting that this system could be further studied for wearable energy device applications. Despite the interesting developed material, it reached some poorer electrochemical results than the previously mentioned works; however, this paper opened the study of flexible supercapacitors utilizing Nb-based electrodes and Na-ion electrolytes, and a few advances have been made since then.

One of those advances, in both flexibles energy devices as well as in supercapacitors in general, was the development in 2019 of a device with a mesoporous Nb_2O_5/carbon nanofiber (CNF) flexible film as anode and graphene framework (GF)/mesoporous CNF as cathode in $NaPF_6$ electrolyte[65]. This research achieved 124 W • h/kg (with 200 W/kg) and a very high 60,000 W/kg (with 55 W • h/kg), both energy and power densities being higher than that of previous results so far. The authors attribute this to the mesoporous nanostructure and to the CNFs, which facilitate both Na^+ and electron transport routes. Besides that, a full-cell device was made using the anode flexible film without the need for binders or additives, which is reasoned to maintain volumetric capacity, and the tested device did not effectively change its capacity when bended, suggesting potential application for portable electronic devices.

The inclusion of other elements with interesting characteristics for energy storage in the electrodes have also been tested. The usage of niobium oxyfluoride wrapped by carbon nanobelts (NBs)[66] as anode is an example, and in this study, through density functional (DFT) calculations, the authors concluded that fluorine-substituted niobium oxyfluoride possesses more energetically favorable sodiation sites and lower diffusion barriers compared to the pristine T-Nb_2O_5, and one of the reasons for this to occur is because of the high electronegativity of fluorine, that can change the electronic structure and create an asymmetry of the electron cloud of the metal, giving rise to more energetically favorable sites for interacting with ions, according to the authors. Although the electrochemical results were not particularly superior to those of the last discussed work, this study presents a remarkable option of material design nonetheless.

Doping is another technique that has been put to use, when sulfur-doped Nb_2O_5 quantum dots uniformly embedded within nitrogen and sulfur co-doped microporous carbon nanofiber that through electrospinning followed by a sulfidation treatment were developed[68]. The resulting fabricated framework increased both electron and Na^+ transport, and the S-doping enhances the electrical conductivity and surface pseudocapacitance through crystalline defect creation.

Out of the discussed systems so far, the one that seems to remain being the one with highest achievements is the 2019 study that used m-Nb_2O_5 CNF and GF/mCNF[65], for having the better properties and being a promising wearable HSC. This study not only developed a niobium based electrode, as it also developed the counter-electrode instead of using a commercial one, which may be a way to further enhance HSCs; and other studies that also developed the counter-electrode[61], if further investigated, may see an increase in their full-cell properties as well. However, such studies, especially those that deal with very specific materials and complex synthesis techniques, should be tested by other researchers to be validated for further use. The same goes for other development techniques that were discussed that still seem very promising, such as defect control, doping, *etc*., even if they didn't achieve immediate better results.

In the energy storage systems described in the works above, organic (non-aqueous) electrolytes are used. However, as previously mentioned, aqueous electrolytes have important advantages such as higher capacitance, lower cost and higher ionic conductivity, when compared to organic electrolytes. As shown below, it is possible to verify that supercapacitors that use the Nb oxide – sodium-ion system can be developed with aqueous electrolytes, as described in the following studies.

Idrees *et al.*[70] synthesized 3D-hollow hierarchical Nb_2O_5 superstructures with orthorhombic phase and tested this material as electrode of asymmetric supercapacitor. The material was obtained by hydrothermal method in a template free synthesis from niobium powder. To build the asymmetric supercapacitor, the authors used activated carbon as cathode and orthorhombic niobium pentoxide (T-Nb_2O_5) as anode. This work was the first to test a niobium-based material in a sodium-ion aqueous electrolyte, using 1 M Na_2SO_4. The authors conducted cyclic voltammetry (CV) and galvanostatic charge-discharge tests to determine the supercapacitor performance. First, each material was individually characterized by cyclic voltammetry to define the potential window, getting to 0 V to -1.1 V (versus Ag/AgCl) to activated carbon and 0 V to +1.2 V (versus Ag/AgCl) for T-Nb_2O_5. The anode made of T- Nb_2O_5 was able to generate a capacitance of 199 F/g for a scan rate of 10 mV/s. According to the authors this energy density was related to redox reaction with reversible nature. The full hybrid device (activated carbon and orthorhombic niobium pentoxide (T-Nb_2O_5)) was able to deliver a specific capacitance of 366 F/g for a current density of 1 A/g in a 2.5 V potential window. Besides, the proposed asymmetric supercapacitor retained 99.68% of the initial capacitance after 2.000 cycles.

Upadhyay *et al.*[12] evaluated the capacitive behavior of nanostructured niobium pentoxide when applied as negative electrode (cathode) in 1 M Na_2SO_4 aqueous electrolyte. Nb_2O_5 nanochannel layers were obtained by anodization of a niobium foil in pure molten ortho-phosphoric acid at 100 ^oC. The oxide was annealed in different temperatures to evaluate the influence of the type of crystalline structure in the resulting capacitance. The electrochemical performance of the electrode was tested by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy in a three-electrode cell. In their best configurations of anodization and annealing treatments, the proposed material was able to reach a capacitance of 100 mF/cm^2 at a current density of 1.3 mA/cm^2 and 81% of this capacitance was retained after 1.500 cycles.

dos Santos Júnior *et al.*[71] obtained sodium and protonic niobates nanowires from hydrothermal synthesis and characterized the electrochemical behavior of these materials in 1 M Na_2SO_4 aqueous electrolyte by cyclic voltammetry. According to the authors, the protonic niobate demonstrated an electrochemical behavior compatible to be applied as material for electrode of electrochemical capacitor. In other work of the group (Sampaio *et al.*[29]), the authors studied the capacitive behavior of highly ordered nanotubular niobium oxide obtained by potentiostatic anodization at room temperature. The study reveals that significant capacitance values (20 mF/cm^2) were achieved for non-crystalline Nb oxide in 1 M Na_2SO_4 aqueous electrolyte. According to the authors, the capacitive behavior was associated with the contribution of two factors: the high specific surface area and the vertically aligned nanotubular morphology that promotes directional transport of ions[29].

On summary, it can be seen that while there have been relatively few works that were made on the topic of niobium-based materials in Na-ion electrolytes, the studies have advanced quite a lot in the last 10 years, with some studies surpassing similar works that utilize Li-ion solutions. Nonetheless, the amount of published research is still small compared to Li-ion application, so authors still have a lot to improve in this field, specially related to non-aqueous electrolytes.

In relation to aqueous electrolytes, it is interesting to point out that the niobium oxide-based material can be used as both, cathode and anode. Besides, a wider potential window than the expected value for aqueous electrolytes can be used, which has direct impact in the amount of energy stored.

It is noticeable that standardization is still an issue in the works mentioned in this review. One of the biggest examples of this is that, even though the subject of the majority of cited works was the development of supercapacitor materials, the concept of capacity was the preferred electrochemical property to be studied and exposed over the concept of capacitance, which was incoherent with the clear capacitor behavior of the devices, well shown in their galvanostatic charge-discharge curves, and capacity is generally a battery property[83,84]. Moreover, always describing which current density was used to achieve each result would be useful to better compare the performance of different materials (a table would be a simple fix for this), and standardization of units should be achieved, because works still haven't settled on which units to always use, in cases such as using A/g or C for current density, F/g or F/cm^2 for specific capacitance and W • h/kg or W • h/cm^3 for energy and power densities. In our opinion, the different units here can reveal different aspects of the same information, so using both as a rule of thumb could be a good choice, but the aforementioned table would be needed even more so that the reader would not be confused with so much information. Furthermore, more attention for calculations should be put into things such as the equivalent series resistance (ESR) of the supercapacitor cell, which must be very low and can be controlled with surface treatments that decrease the ohmic drop at the current collector/active material interface[8].

In the cited studies in this review, materials were typically composed of conductive material and niobium oxide composites, and further exploration of doping or insertion of elements to increase conductivity can still be made. It is interesting to note a gap in SC studies that is the use of materials other than Nb_2O_5, such as titanium-niobium oxides, that have a higher theoretical capacity (388~401 mA • h/g), another redox pair involved (Ti^{4+}/Ti^{3+} around 2.0 V[78]) and have been explored in SIB applications[85-87]. Doping using more elements, such as antimony[88], which has a very high theoretical capacity but with inherent large volumetric expansion, can also be studied for SCs. The application of the supercapacitors systems mentioned in this review on flexible devices is also very promising and can be further studied. At this stage of studies, one of the upcoming challenges should be to develop niobium-based electrodes that can be easily fabricated and maintain some of the best achieved properties so far, given that right now the development of many of many of the cited materials is fairly complex. So researchers should set the goal to have an electrode that is more compatible with large scale production, which will also imply in having more standardized tests and tests for specific applications, and studying secondary effects, such as the self-discharge rate of the supercapacitor.

4. Conclusions and Outlook

Among the various active materials and electrolytes studied for energy storage devices, electrodes made of oxides containing niobium and electrolytes based on sodium-ion have emerged as highly promising systems for electrochemical energy storage. In this scene, non-aqueous electrolytes are widely more used to assemble the Nb oxide - sodium-ion sets. For these systems, the energy storage is controlled by the mechanism of intercalation/deintercalation of sodium-ions in the oxide structure. There have been many improvements over pristine Nb_2O_5, especially concerning its low electric conductivity, and generally consisted of developing composites or core@shell systems with highly conductive materials (especially carbon-based) or doping to enhance electrochemical properties (with elements such as sulfur or fluorine). The development of such materials, however, comes with the disadvantage of more elaborate synthesis processes, so that one of the most noticeable challenges on this field is to make the electrode fabrication feasible for manufacturing and commercialization, and the overcoming of such challenge will be to researchers focus more and more on simpler material obtaining routes, such as hydrothermal synthesis, given that some of the discussed techniques are still fairly complex. On the other hand, research on aqueous electrolytes is still limited; nonetheless, it has yielded promising results, including an extended potential window beyond the typical values for such electrolytes. Hence, there is a highly promising prospect for research involving Nb oxides in aqueous electrolytes, particularly due to the potential for exploring Nb oxides as both cathodes and anodes in aqueous electrolytes.

Finally, in terms of constructing full cell devices utilizing the Nb oxide - sodium-ion system, carbon-based materials are commonly employed as the counter-electrode. However, there is plenty of space for the use of other materials as counter-electrode, such as other oxides. This strategy could potentially enhance the efficiency, performance, and versatility of these devices, offering new ways for advancements in energy storage technologies. Through diversifying the range of electrode materials, researchers can unlock innovative possibilities and pave the way for further breakthroughs in sodium-ion battery technology.

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Consent for publication

The authors declare that they have secured consent for the publication of the content of this review.

Availability of Supporting Data

Not applicable.

Conflict of Interest

No conflict of interest to declare.

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[1] Barnhart CJ, Dale M, Brandt AR, *et al.* The energetic implications of curtailing versus storing solar-and wind-generated electricity. *Energy & Environmental Science*, 2013;6(10):2804-2810. https://doi.org/10.1039/C3EE41973H

[2] Hannan MA, Hoque MM, Mohamed A, *et al.* Review of energy storage systems for electric vehicle applications: issues and challenges. *Renewable and Sustainable Energy Reviews*, 2017;69:771-789. https://doi.org/10.1016/j.rser.2016.11.171

[3] Tamor MA and Stechel EB. Electrification of transportation means a lot more than a lot more electric vehicles. *Iscience*, 2022;25(6):104376. https://doi.org/10.1016/j.isci.2022.104376

[4] Liang Y, Zhao CZ, Yuan H, *et al.* A review of rechargeable batteries for portable electronic devices. *InfoMat*, 2019;1(1):6-32. https://doi.org/10.1002/inf2.12000

[5] Chen W, Liang J, Yang Z, *et al.* A review of lithium-ion battery for electric vehicle applications and beyond. *Energy Procedia*, 2019;158:4363-4368. https://doi.org/10.1016/j.egypro.2019.01.783

[6] Şahin ME, Blaabjerg F and Sangwongwanich A. A comprehensive review on supercapacitor applications and developments. *Energies*, 2022;15(3):674. https://doi.org/10.3390/en15030674

[7] Kötz R and Carlen M. Principles and applications of electrochemical capacitors. *Electrochimica Acta*, 2000;45(15-16):2483-2498. https://doi.org/10.1016/S0013-4686(00)00354-6

[8] González A, Goikolea E, Barrena JA, *et al.* Review on supercapacitors: technologies and materials. *Renewable and Sustainable Energy Reviews*, 2016;58:1189-1206. https://doi.org/10.1016/j.rser.2015.12.249

[9] Beguin F, Frackowiak E and Lu M, Supercapacitors: materials, systems and applications. Wiley-VCH, Weinheim; 2012. https://doi.org/10.1002/9783527646661

[10] Brezesinski K, Wang J, Haetge J, *et al.* Pseudocapacitive contributions to charge storage in highly ordered mesoporous group V transition metal oxides with iso-oriented layered nanocrystalline domains. *Journal of the American Chemical Society*, 2010;132(20):6982-6990. https://doi.org/10.1021/ja9106385

[11] Yi TF, Sari HMK, Li X, *et al.* A review of niobium oxides based nanocomposites for lithium-ion batteries, sodium-ion batteries and supercapacitors. *Nano Energy*, 2021;85:105955. https://doi.org/10.1016/j.nanoen.2021.105955

[12] Upadhyay KK, Cha G, Hildebrand H, *et al.* Capacitance response in an aqueous electrolyte of Nb_2O_5 nanochannel layers anodically grown in pure molten o-H_3PO_4. *Electrochimica Acta*, 2018;281:725-737. https://doi.org/10.1016/j.electacta.2018.06.014

[13] Gomes MAB, Bulhões LOS, De Castro SC, *et al.* The electrochromic process at Nb_2O_5 electrodes prepared by thermal oxidation of Niobium. *Journal of the Electrochemical Society*, 1990;137(10):3067. https://doi.org/10.1149/1.2086161

[14] Thangavel R, Ganesan BK, Thangavel V, *et al.* Emerging materials for sodium-ion hybrid capacitors: a brief review. *ACS Applied Energy Materials*, 2021;4(12):13376-13394. https://doi.org/10.1021/acsaem.1c02099

[15] Yabuuchi N, Kubota K, Dahbi M, *et al.* Research development on sodium-ion batteries. *Chemical Reviews*, 2014;114(23):11636-11682. https://doi.org/10.1021/cr500192f

[16] Conway BE. Electrochemical supercapacitors. 1st ed. Boston: Springer; 1999. http://dx.doi.org/10.1007/978-1-4757-3058-6

[17] Conway BE and Gileadi E. Kinetic theory of pseudo-capacitance and electrode reactions at appreciable surface coverage. *Transactions of the Faraday Society*, 1962;58:2493-2509. https://doi.org/10.1039/TF9625802493

[18] Fleischmann S, Mitchell JB, Wang R, *et al.* Pseudocapacitance: from fundamental understanding to high power energy storage materials. *Chemical Reviews*, 2020;120(14):6738-6782. https://doi.org/10.1021/acs.chemrev.0c00170

[19] Augustyn V, Simon P and Dunn B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy & Environmental Science*, 2014;7(5):1597-1614. https://doi.org/10.1039/C3EE44164D

[20] Liu Y, Jiang SP and Shao Z. Intercalation pseudocapacitance in electrochemical energy storage: recent advances in fundamental understanding and materials development. *Materials Today Advances*, 2020;7:100072. https://doi.org/10.1016/j.mtadv.2020.100072

[21] Chang BY, Ahn E and Park SM. Real-time staircase cyclic voltammetry fourier transform electrochemical impedance spectroscopic studies on underpotential deposition of lead on gold. *The Journal of Physical Chemistry C*, 2008;112(43):16902-16909. https://doi.org/10.1021/jp805960j

[22] Lou S, Cheng X, Wang L, *et al.* High-rate capability of three-dimensionally ordered macroporous T-Nb_2O_5 through Li^+ intercalation pseudocapacitance. *Journal of Power Sources*,

2017;361:80-86.
https://doi.org/10.1016/j.jpowsour.2017.06.023

[23] Chen C, Wen Y, Hu X, *et al.* Na^+ intercalation pseudocapacitance in graphene-coupled titanium oxide enabling ultra-fast sodium storage and long-term cycling. *Nature Communications*, 2015;6(1):6929.
https://doi.org/10.1038/ncomms7929

[24] Wei Q, Huang T, Huang X, *et al.* High-rate sodium-ion storage of vanadium nitride via surface-redox pseudocapacitance. *Interdisciplinary Materials*, 2023;2(3):434-442.
https://doi.org/10.1002/idm2.12080

[25] Zhao S, Liu Z, Xie G, *et al.* Achieving high-performance 3D K^+-pre-intercalated $Ti_3C_2T_x$ MXene for potassium-ion hybrid capacitors via regulating electrolyte solvation structure. *Angewandte Chemie International Edition*, 2021;60(50):26246-26253.
https://doi.org/10.1002/anie.202112090

[26] Reeves KG, Ma J, Fukunishi M, *et al.* Insights into Li^+, Na^+, and K^+ intercalation in lepidocrocite-type layered TiO_2 structures. *ACS Applied Energy Materials*, 2018;1(5):2078-2086.
https://doi.org/10.1021/acsaem.8b00170

[27] Xu Z, Liu Y, Zhou W, *et al.* B-site cation-ordered double-perovskite oxide as an outstanding electrode material for supercapacitive energy storage based on the anion intercalation mechanism. *ACS Applied Materials & Interfaces*, 2018;10(11):9415-9423.
https://doi.org/10.1021/acsami.7b19391

[28] Che W, Wei M, Sang Z, *et al.* Perovskite $LaNiO_{3-\delta}$ oxide as an anion-intercalated pseudocapacitor electrode. *Journal of Alloys and Compounds*, 2018;731:381-388.
https://doi.org/10.1016/j.jallcom.2017.10.027

[29] Sampaio EJP, Antonini LM, dos Santos Júnior AG, *et al.* Highly ordered nanotubular niobium oxide obtained by self-organizing anodization: a study of capacitive behavior. *Ceramics International*, 2022;48(17):25424-25430.
https://doi.org/10.1016/j.ceramint.2022.05.219

[30] Wang Z, Su H, Liu F, *et al.* Establishing highly-efficient surface faradaic reaction in flower-like $NiCo_2O_4$ nano-/micro-structures for next-generation supercapacitors. *Electrochimica Acta*, 2019;307:302-309.
https://doi.org/10.1016/j.electacta.2019.03.227

[31] Pandolfo AG and Hollenkamp AF. Carbon properties and their role in supercapacitors. *Journal of Power Sources*, 2006;157(1):11-27.
https://doi.org/10.1016/j.jpowsour.2006.02.065

[32] Gu W and Yushin G. Review of nanostructured carbon materials for electrochemical capacitor applications: advantages and limitations of activated carbon, carbide-derived carbon, zeolite-templated carbon, carbon aerogels, carbon nanotubes, onion-like carbon, and graphene. *Wiley Interdisciplinary Reviews: Energy and Environment*, 2014;3(5):424-473.
https://doi.org/10.1002/wene.102

[33] Liang R, Du Y, Xiao P, *et al.* Transition metal oxide electrode materials for supercapacitors: a review of recent developments. *Nanomaterials*, 2021;11(5):1248.
https://doi.org/10.3390/nano11051248

[34] Abdah MAAM and Azman NHN, Kulandaivalu S, *et al.* Review of the use of transition-metal-oxide and conducting polymer-based fibres for high-performance supercapacitors. *Materials & Design*, 2020;186:108199.
https://doi.org/10.1016/j.matdes.2019.108199

[35] Breitkopf C and Swider-Lyons K. Springer handbook of electrochemical energy. 1st ed. Berlin: Springer; 2017.
https://doi.org/10.1007/978-3-662-46657-5

[36] Kim JW, Augustyn V and Dunn B. The effect of crystallinity on the rapid pseudocapacitive response of Nb_2O_5. *Advanced Energy Materials*, 2012;2(1):141-148.
https://doi.org/10.1002/aenm.201100494

[37] Ramachandran R and Wang F. Electrochemical capacitor performance: influence of aqueous electrolytes. 1st ed. In: Liudvinavičius L (editor). Supercapacitors-theoretical and practical solutions. London: IntechOpen; 2018. p. 51-68.
https://doi.org/10.5772/intechopen.70694

[38] Wu X, Yang H, Yu M, *et al.* Design principles of high-voltage aqueous supercapacitors. *Materials Today Energy*, 2021;21:100739.
https://doi.org/10.1016/j.mtener.2021.100739

[39] Endo M, Takeda T, Kim YJ, *et al.* High power electric double layer capacitor (EDLC's); from

operating principle to pore size control in advanced activated carbons. *Carbon Letters*, 2001;1(3_4):117-128.

[40] Zhong C, Deng Y, Hu W, *et al.* A review of electrolyte materials and compositions for electrochemical supercapacitors. *Chemical Society Reviews*, 2015;44(21):7484-7539. https://doi.org/10.1039/C5CS00303B

[41] Liu M, Ao H, Jin Y, *et al.* Aqueous rechargeable sodium ion batteries: Developments and prospects. *Materials Today Energy*, 2020;17:100432. https://doi.org/10.1016/j.mtener.2020.100432

[42] Fic K, Lota G, Meller M, *et al.* Novel insight into neutral medium as electrolyte for high-voltage supercapacitors. *Energy & Environmental Science*, 2012;5(2):5842-5850. https://doi.org/10.1039/C1EE02262H

[43] Liu Y, Wang Z, Veder JPM, *et al.* Highly defective layered double perovskite oxide for efficient energy storage via reversible pseudocapacitive oxygen-anion intercalation. *Advanced Energy Materials*, 2018;8(11):1702604. https://doi.org/10.1002/aenm.201702604

[44] Ramasamy HV, Kaliyappan K, Thangavel R, *et al.* Efficient method of designing stable layered cathode material for sodium ion batteries using aluminum doping. *The Journal of Physical Chemistry Letters*, 2017;8(20):5021-5030. https://doi.org/10.1021/acs.jpclett.7b02012

[45] Thangavel R, Samuthira Pandian A, Ramasamy HV, *et al.* Rapidly synthesized, few-layered pseudocapacitive SnS_2 anode for high-power sodium ion batteries. *ACS Applied Materials & Interfaces*, 2017;9(46):40187-40196. https://doi.org/10.1021/acsami.7b11040

[46] Chen Z, Augustyn V, Jia X, *et al.* High-performance sodium-ion pseudocapacitors based on hierarchically porous nanowire composites. *ACS Nano*, 2012;6(5):4319-4327. https://doi.org/10.1021/nn300920e

[47] Zhang Y, Jiang J, An Y, *et al.* Sodium-ion capacitors: materials, mechanism, and challenges. *ChemSusChem*, 2020;13(10):2522-2539. https://doi.org/10.1002/cssc.201903440

[48] Kuratani K, Yao M, Senoh H, *et al.* Na-ion capacitor using sodium pre-doped hard carbon and activated carbon. *Electrochimica Acta*, 2012;76:320-325. https://doi.org/10.1016/j.electacta.2012.05.040

[49] Ajuria J, Redondo E, Arnaiz M, *et al.* Lithium and sodium ion capacitors with high energy and power densities based on carbons from recycled olive pits. *Journal of Power Sources*, 2017;359:17-26. https://doi.org/10.1016/j.jpowsour.2017.04.107

[50] Kado Y and Soneda Y. MgO-templated carbon as a negative electrode material for Na-ion capacitors. *Journal of Physics and Chemistry of Solids*, 2016;99:167-172. https://doi.org/10.1016/j.jpcs.2016.08.021

[51] Wang R, Wang S, Peng X, *et al.* Elucidating the intercalation pseudocapacitance mechanism of MoS_2–carbon monolayer interoverlapped superstructure: toward high-performance sodium-ion-based hybrid supercapacitor. *ACS Applied Materials & Interfaces*, 2017;9(38):32745-32755. https://doi.org/10.1021/acsami.7b09813

[52] Li Y, Wang H, Wang L, *et al.* Ultrafast Na^+-storage in TiO_2-coated MoS_2@ N-doped carbon for high-energy sodium-ion hybrid capacitors. *Energy Storage Materials*, 2019;23:95-104. https://doi.org/10.1016/j.ensm.2019.05.024

[53] Cui J, Yao S, Lu Z, *et al.* Revealing pseudocapacitive mechanisms of metal dichalcogenide SnS_2/graphene-CNT aerogels for high-energy Na hybrid capacitors. *Advanced Energy Materials*, 2018;8(10):1702488. https://doi.org/10.1002/aenm.201702488

[54] Le Z, Liu F, Nie P, *et al.* Pseudocapacitive sodium storage in mesoporous single-crystal-like TiO_2-graphene nanocomposite enables high-performance sodium-ion capacitors. *ACS Nano*, 2017;11(3):2952-2960. https://doi.org/10.1021/acsnano.6b08332

[55] Zhu YE, Yang L, Sheng J, *et al.* Fast sodium storage in TiO_2@CNT@C nanorods for high-performance Na-ion capacitors. *Advanced Energy Materials*, 2017;7(22):1701222. https://doi.org/10.1002/aenm.201701222

[56] Babu B and Shaijumon MM. High performance sodium-ion hybrid capacitor based on $Na_2Ti_2O_4(OH)_2$ nanostructures. *Journal of Power Sources*, 2017;353:85-94. https://doi.org/10.1016/j.jpowsour.2017.03.143

[57] Thangavel R, Kaliyappan K, Kim DU, *et al.* All-

organic sodium hybrid capacitor: a new, high-energy, high-power energy storage system bridging batteries and capacitors. *Chemistry of Materials*, 2017;29(17):7122-7130. https://doi.org/10.1021/acs.chemmater.7b00841

[58] Thangavel R, Ponraj R, Kannan AG, *et al.* High performance organic sodium-ion hybrid capacitors based on nano-structured disodium rhodizonate rivaling inorganic hybrid capacitors. *Green Chemistry*, 2018;20(21):4920-4931. https://doi.org/10.1039/C8GC01987H

[59] Ding J, Hu W, Paek E, *et al.* Review of hybrid ion capacitors: from aqueous to lithium to sodium. *Chemical Reviews*, 2018;118(14):6457-6498. https://doi.org/10.1021/acs.chemrev.8b00116

[60] Lim E, Jo C, Kim MS, *et al.* High-performance sodium-ion hybrid supercapacitor based on Nb_2O_5@carbon core-shell nanoparticles and reduced graphene oxide nanocomposites. *Advanced Functional Materials*, 2016;26(21):3711-3719. https://doi.org/10.1002/adfm.201505548

[61] Li H, Zhu Y, Dong S, *et al.* Self-assembled Nb_2O_5 nanosheets for high energy-high power sodium ion capacitors. *Chemistry of Materials*, 2016;28(16):5753-5760. https://doi.org/10.1021/acs.chemmater.6b01988

[62] Tong Z, Liu S, Zhou Y, *et al.* Rapid redox kinetics in uniform sandwich-structured mesoporous Nb_2O_5/graphene/mesoporous Nb_2O_5 nanosheets for high-performance sodium-ion supercapacitors. *Energy Storage Materials*, 2018;13:223-232. https://doi.org/10.1016/j.ensm.2017.12.005

[63] Wu Y, Fan X, Gaddam RR, *et al.* Mesoporous niobium pentoxide/carbon composite electrodes for sodium-ion capacitors. *Journal of Power Sources*, 2018;408:82-90. https://doi.org/10.1016/j.jpowsour.2018.10.080

[64] Wang X, Li Q, Zhang L, *et al.* Caging Nb_2O_5 nanowires in PECVD-derived graphene capsules toward bendable sodium-ion hybrid supercapacitors. *Advanced Materials*, 2018;30(26):1800963. https://doi.org/10.1002/adma.201800963

[65] Li Y, Wang H, Wang L, *et al.* Mesopore-induced ultrafast Na^+-storage in T-Nb_2O_5/carbon nanofiber films toward flexible high-power Na-ion capacitors. *Small*, 2019;15(9):1804539. https://doi.org/10.1002/smll.201804539

[66] Wu Y, Fan X, Chen Y, *et al.* Fluorine substitution enabling pseudocapacitive intercalation of sodium ions in niobium oxyfluoride. *Journal of Materials Chemistry A*, 2019;7(36):20813-20823. https://doi.org/10.1039/C9TA07320E

[67] Jia R, Jiang Y, Li R, *et al.* Nb_2O_5 nanotubes on carbon cloth for high performance sodium-ion capacitors. *Science China Materials*, 2020;63(7):1171-1181. https://doi.org/10.1007/s40843-020-1278-9

[68] She L, Li Q, Zhang F, *et al.* Sulfur doping induced anionic oxidation of niobium-pentoxide-based anode for ultralong-life and high energy-density Na-ion capacitors. *Journal of Power Sources*, 2020;451:227744. https://doi.org/10.1016/j.jpowsour.2020.227744

[69] Real CG, Thaines EHNS, Pocrifka LA, *et al.* Freestanding niobium pentoxide-decorated multiwalled carbon nanotube electrode: Charge storage mechanism in sodium-ion pseudocapacitor and battery. *Journal of Energy Storage*, 2022;52:104793. https://doi.org/10.1016/j.est.2022.104793

[70] Idrees F, Hou J, Cao C, *et al.* Template-free synthesis of highly ordered 3D-hollow hierarchical Nb_2O_5 superstructures as an asymmetric supercapacitor by using inorganic electrolyte. *Electrochimica Acta*, 2016;216:332-338. https://doi.org/10.1016/j.electacta.2016.09.031

[71] dos Santos Júnior AG, Antonini LM, Sampaio EJP, *et al.* Sodium niobates and protonic niobates nanowires obtained from hydrothermal synthesis: electrochemical behavior in aqueous electrolyte. *Ceramics International*, 2022;48(2):1522-1531. https://doi.org/10.1016/j.ceramint.2021.09.230

[72] Deng Q, Fu Y, Zhu C, *et al.* Niobium-based oxides toward advanced electrochemical energy storage: recent advances and challenges. *Small*, 2019;15(32):1804884. https://doi.org/10.1002/smll.201804884

[73] Viet AL, Reddy MV, Jose R, *et al.* Nanostructured Nb_2O_5 polymorphs by electrospinning for rechargeable lithium batteries. *The Journal of Physical Chemistry C*, 2010;114(1):664-671. https://doi.org/10.1021/jp9088589

[74] Yan L, Rui X, Chen G, *et al.* Recent advances in nanostructured Nb-based oxides for

electrochemical energy storage. *Nanoscale*, 2016;8(16):8443-8465. https://doi.org/10.1039/C6NR01340F

[75] Ge H, Li N, Li D, *et al.* Study on the theoretical capacity of spinel lithium titanate induced by low-potential intercalation. *The Journal of Physical Chemistry C*, 2009;113(16):6324-6326. https://doi.org/10.1021/jp9017184

[76] Madian M, Eychmüller A and Giebeler L. Current advances in TiO_2-based nanostructure electrodes for high performance lithium ion batteries. *Batteries*, 2018;4(1):7. https://doi.org/10.3390/batteries4010007

[77] Chen D, Wang JH, Chou TF, *et al.* Unraveling the nature of anomalously fast energy storage in T-Nb_2O_5. *Journal of the American Chemical Society*, 2017;139(20):7071-7081. https://doi.org/10.1021/jacs.7b03141

[78] Hu L, Luo L, Tang L, *et al.* $Ti_2Nb_{2x}O_{4+5x}$ anode materials for lithium-ion batteries: a comprehensive review. *Journal of Materials Chemistry A*, 2018;6(21):9799-9815. https://doi.org/10.1039/C8TA00895G

[79] Nico C, Monteiro T and Graça MPF. Niobium oxides and niobates physical properties: review and prospects. *Progress in Materials Science*, 2016;80:1-37. https://doi.org/10.1016/j.pmatsci.2016.02.001

[80] Lim E, Kim H, Jo C, *et al.* Advanced hybrid supercapacitor based on a mesoporous niobium pentoxide/carbon as high-performance anode. *ACS Nano*, 2014;8(9):8968-8978. https://doi.org/10.1021/nn501972w

[81] Kim H, Lim E, Jo C, *et al.* Ordered-mesoporous Nb_2O_5/carbon composite as a sodium insertion material. *Nano Energy*, 2015;16:62-70. https://doi.org/10.1016/j.nanoen.2015.05.015

[82] Yan L, Chen G, Sarker S, *et al.* Ultrafine Nb_2O_5 nanocrystal coating on reduced graphene oxide as anode material for high performance sodium ion battery. *ACS Applied Materials & Interfaces*, 2016;8(34):22213-22219. https://doi.org/10.1021/acsami.6b06516

[83] Da Silva LM, Cesar R, Moreira CMR, *et al.* Reviewing the fundamentals of supercapacitors and the difficulties involving the analysis of the electrochemical findings obtained for porous electrode materials. *Energy Storage Materials*, 2020;27:555-590. https://doi.org/10.1016/j.ensm.2019.12.015

[84] Xie J, Yang P, Wang Y, *et al.* Puzzles and confusions in supercapacitor and battery:theory and solutions. *Journal of Power Sources*, 2018;401:213-223. https://doi.org/10.1016/j.jpowsour.2018.08.090

[85] Xie K, Wei W, Yu H, *et al.* Use of a novel layered titanoniobate as an anode material for long cycle life sodium ion batteries. *RSC Advances*, 2016;6(42):35746-35750. https://doi.org/10.1039/C6RA02530G

[86] Li S, Cao X, Schmidt CN, *et al.* $TiNb_2O_7$/graphene composites as high-rate anode materials for lithium/sodium ion batteries. *Journal of Materials Chemistry A*, 2016;4(11):4242-4251. https://doi.org/10.1039/C5TA10510B

[87] Shen L, Wang Y, Lv H, *et al.* Ultrathin $Ti_2Nb_2O_9$ nanosheets with pseudocapacitive properties as superior anode for sodium-ion batteries. *Advanced Materials*, 2018;30(51):1804378. https://doi.org/10.1002/adma.201804378

[88] Wang L, Bi X and Yang S. Synergic antimony-niobium pentoxide nanomeshes for high-rate sodium storage. *Journal of Materials Chemistry A*, 2018;6(15):6225-6232. https://doi.org/10.1039/C8TA01130C