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Nanofeather ruthenium nitride electrodes for electrochemical capacitors

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ABSTRACT

Fast charging is a critical concern for the next generation of electrochemical energy storage devices, driving extensive research on new electrode materials for electrochemical capacitors and micro-supercapacitors. Herein, we introduce a significant advance in producing thick ruthenium nitride (RuN) pseudocapacitive films, based on a sputter deposition method. These RuN films deliver over 0.8 $F.cm^{-2}$ (~ 500 $F.cm^{-3}$) with a time constant below 6 seconds. By utilizing an original electrochemical oxidation process, the volumetric capacitance doubles (1200 $F.cm^{-3}$) without sacrificing cycling stability. This enables an extended operating potential window up to 0.85 V vs Hg/HgO, resulting in a boost to 3.2 $F.cm^{-2}$ (3200 $F.cm^{-3}$). *Operando* X-ray absorption spectroscopy and transmission electron microscopy analyses reveal novel insights into the electrochemical oxidation process. The charge storage mechanism takes advantage of the high electrical conductivity and the morphology of cubic RuN and Ru phases in the feather-like core, leading to high electrical conductivity in combination with high capacity. Accordingly, we have developed an analysis which relates capacity to time constant as a means of identifying materials capable of retaining high capacity at high charge-discharge rates.

The ever-escalating climate crisis has heightened the importance of energy scavenging and storage, necessitating significant future shifts in societal customs and habits toward effective energy management. Irrespective of the scale considered (macro or millimeter scales), the energy needs to be efficiently harvested, stored and distributed at different charging and discharging regimes. For instance, fast charging is crucial for the next generation of miniaturized electronic devices that play a critical role in the ever-expanding Internet of Things (IoT) and next-generation electronics [1,2]. Electrochemical capacitors (ECs) and micro-supercapacitors (MSCs) continue to be studied extensively for efficient and self-sustaining fast-charging devices [1,3] for IoT applications in various fields (e-medicine, defense, structural health monitoring, and animal tracking). These miniaturized power sources can be broadly categorized into two types based on their electrode materials: electrical double layer capacitors (EDLCs) and pseudocapacitors [4]. EDLCs store charge via an electrostatic charge absorption mechanism at the electrode/electrolyte interface in nanoporous carbon electrodes, while pseudocapacitors store charge through fast redox reactions at the surface or sub-surface without phase transformation of the electrode material [5].

Although transition metal oxides have been investigated as possible pseudocapacitive materials, their applications in thin film electrochemical energy storage devices are limited due to either low electrical conductivity or low specific capacitance. Transition metal nitrides (TMNs), however, have been identified as potential candidate materials. In addition to significant specific capacitance (> 700 $F.cm^{-3}$), their high electrical conductivity enables TMN electrodes to also serve as the current collector in EC and MSCs. Following the pioneering work of Conway on molybdenum nitride thin films[6] and Kumta's results on nanostructured vanadium nitride particles[7], numerous TMNs have emerged as highly efficient pseudocapacitive electrode materials for ECs and MSCs, including VN[8–10], TiN[11,12], NbN[13], Mo_2N[14], W_2N[15] and CrN[16,17]. Charge storage in these materials arises from charge transfer between the TMN and hydroxide ions or protons in the electrolyte. While VN, Mo_2N, W_2N electrode materials provide remarkable capacitance value in alkaline electrolyte, their working potential window is restricted to ~ 0.6 V. In a symmetric EC based on TMNs, only half of the potential window is used in each electrode (0.3 V for each electrode). In our recent studies[18], we demonstrated that VN and hydrous RuO_2 (h-RuO_2) could be combined in an asymmetric configuration in 1M KOH (cell voltage ~ 1.2 V): performance was limited (< 0.2 $F.cm^{-2}$) by the thickness of the electrodeposited h-RuO_2. These results underscore the importance of finding a positive electrode material with high specific capacitance to be used in combination with a VN negative electrode.

The present paper describes how ruthenium nitride (RuN) films is an interesting positive electrode material for asymmetric MSC or EC. The properties of RuN are largely unexplored although initial research showed promising electrochemical properties despite difficulties in stabilizing the RuN phase in bulk materials[19,20]. We have successfully addressed this issue through magnetron sputtered RuN films. The morphology of the electrode material plays a crucial role in determining its capacitance and rate capability [21–24]. Nanofeather morphology [25,26], with its high specific surface area, provides more active sites for fast redox reactions and facilitates efficient electrolyte ion diffusion in ‘porous’ materials. Additionally, short diffusion pathways permit faster ion transport between the electrolyte and the active material, enabling rapid charge/discharge and thus high rate performance.

The tuning of electrode morphology to facilitate fast ion diffusion and better ion accessibility in pseudocapacitive material is essential to deliver high capacitance at high rate [21,27–30]. Vacuum deposition methods provide an exciting arena for tuning the properties of TMN pseudocapacitive films [9,24,31,32]. It also serves as a practical tool for the synthesis of model materials without the need for any conductive additives and/or binders, making it suitable for probing the intrinsic properties of material. In addition, films with various morphologies can be deposited by magnetron sputtering, allowing for the evaluation of the structure – property relationships of thin film materials. Beyond TMNs such as VN, MoN and WN[6,9,15], ruthenium oxide films can also be prepared by magnetron sputter deposition methods and have been evaluated for miniaturized electrochemical capacitors, thus enabling the fabrication of micro-supercapacitors based on ruthenium nitride, oxide or oxynitride electrodes. Schematically, depending on the synthesis conditions[33], three different 'families' of pseudocapacitive films can be distinguished (**Fig. 1**):

The first family (*F1*, **Fig. 1**) comprises dense (compact) films consisting of large grains (grain size > 1000 nm), wherein grain boundaries act as the contact surface between the liquid electrolyte and the electroactive material. *F1* suffers from a low specific surface area that restricted mostly the interaction between the electrode material and the ions at the top surface — as recently observed for example in dense sputtered $FeWO_4$ thin films [34]. Due to the low ion diffusion and accessibility within this dense electrode material, poor performance with limited capacitance are obtained (C~ 11 $F.cm^{-3}$, $\tau \sim 5$ s).

The second family (*F2*) involves columnar materials, where the pseudocapacitive electrode (*F2*, **Fig. 1**) consists of straight yet dense columns with tunable column diameter (~100 nm) and spacing (as observed for example in $MnFe_2O_4$ films) [10,35]. *F2* thus benefits from increased interaction between the redox active material and the electrolyte ions, significantly enhancing electrode capacitance (C~ 50 F.cm^{-3}). This F2 family, however, exhibits large column diameters leading to limited ion diffusion — this also hinders electron transport, thereby reducing overall electrode performance with long time constant (τ ~ 250 s).

The focus of this paper is on the last family (*F3*, **Fig. 1**), and concerns the design of advanced TMN films that optimize both ion diffusion and accessibility, benefitting from the high electrical conductivity of TMN. Specifically, we propose RuN films exhibiting a nanofeather morphology [36] that facilitates ion diffusion within the 'nanoporous' material, thus enhancing interactions between the electroactive TMN and the ions (C ~ 500 F.cm^{-3}, τ ~ 3 s). Additionally, we leverage the high conductivity of the TMN 'scaffold' to maximize the rate capability of thick electrode materials (> 5-10 µm) [9,10].

The STEM HAADF (high angle annular dark field) cross-section imaging (**Fig. 2a**) shows the desired feather-like morphology. For a ~550 nm-thick RuN film, the feather exhibits a diameter of ~30 nm, in agreement with predictions for the *F3* family (nanofeather films). XRD analysis (**Fig. 2b**) reveals the coexistence of two cubic Fm-3m Ru and RuN phases. The diffraction peaks at 2θ = 40.5°, 47°, 68° and 83.1° correspond to the (111), (200), (220) and (311) lattice planes of the cubic Fm-3m Ru phase. A further set of diffraction peaks at 2θ ~35.2°, 41°, 71° and 89 ° are attributed to the cubic Fm-3m RuN phase, corresponding to the (111), (020), (131) and (040) lattice planes, respectively. The coexistence of these two cubic phases will be strengthened by the results proposed in **Fig. 3**. Notably, no crystallized RuO_2 or ruthenium oxynitride phases were detected via XRD. High-resolution TEM images (**Fig. S1**) reveal the presence of crystallized domains: the measured inter-reticular distances align with those of RuN cubic phases $d_{102}(1) = 1.93$ Å $d_{102}(2) = 2.03$ Å, $d_{020}(1) = 2.16$ Å $d_{020}(2) = 2.28$ Å. The high-resolution XPS spectra of the Ru *3p* core level in **Fig. 2c & S2** show the surface analyses and depth profiles after etching for 1, 5 and 10 minutes, respectively. The Ru *3p* core level XPS analysis *vs* etching time (**Fig. 2c**) demonstrates two sets of peaks, Ru $3p_{1/2}$ and Ru $3p_{3/2}$ at ~483 and ~460 eV, respectively. Each peak could be fit with three contributions corresponding to the Ru^0, RuO_2 and RuN bands. For the Ru $3p_{3/2}$ core level, the first contribution at ~460.9 eV can be attributed to Ru^0, while the second contribution at 463.5 eV corresponds to RuO_2. A third contribution at ~465-466 eV can be ascribed to a nitride RuN specie. A similar approach can be applied to the Ru $3p_{3/2}$ core level peak at ~483 eV. Thus, regardless of etching time, Ru, RuO_2 and RuN species are consistently present. The conclusions drawn from XPS were further confirmed by GDOES depth profiles and STEM EDS analyses of the film in cross-sections (**Fig. 2d and Fig. S2**). Additional comments are available in supplementary information (XPS, GDOES and morphology analyses of the RuN film section**)**. XRD analysis of RuN films (**Fig. 3a**) proves that diffraction peaks can be assigned to the two cubic Ru and RuN phases.

The electrochemical performance of RuN films was evaluated, focusing on electrode behavior *vs* film thickness, as reported in **Fig. 3** and **Fig. S4-S5**. In addition, RuN electrodes were tested in various electrolytes in order to determine the best tradeoff between capacitance values and cycling stability. **Fig. S4a-f** reports on the electrochemical performance of RuN films in 0.5M H_2SO_4, 1M LiOH, 1M $LiNO_3$ and 1M Na_2SO_4 aqueous electrolytes while **Fig. S4g-k** shows more detailed studies (see in supplementary information, electrochemical testing of sputtered RuN films in various electrolytes section) in 1M KOH and 0.5M H_2SO_4. Lastly, **Fig. S5** are devoted to the performance of RuN electrodes vs the film thickness.

The cyclic voltammetry (CV) curves for RuN in 1M KOH (**Fig. 3b** and **Figs. S5a-d)** systematically exhibit the rectangular voltammograms typical of pseudocapacitive materials [28,29]. The RuN maintains its electrochemical signature even at higher scan rates, suggesting a high rate capability which can be attributed to the nanofeather morphology and high electrical conductivity. The volumetric capacitance of thick RuN films (**Fig. 3c** and **Fig. S5e**) varies from 600 to 460 $F.cm^{-3}$. The nearly constant value of the surface capacitance *vs* scan rate plot reaffirms the remarkable rate capability of the RuN electrode. The 16 µm-thick RuN film loses only 24% of its initial capacitance ($C_{surface}$~0.75 $F.cm^{-2}$) as the scan rate increases from 2 to 100 $mV.s^{-1}$ (cycling time = 5.5 s). This value decreases to 18% for the 5 µm-thick RuN film.

The kinetic limitations within the RuN electrodes were investigated using the Trasatti method[24,37,38] (see details in Supplementary information, Trasatti fitting of the RuN films vs thickness section). The fitting results in **Fig. 3d** summarize the performance vs RuN thickness. For thin RuN layers (~0.6 µm-thick), C_{total}, $C_{outer-surface}$ and $C_{surface}$ measured at 2 $mV.s^{-1}$ are at the same order of magnitude, highlighting the intriguing performance of the RuN electrode. Thicker films clearly demonstrate remarkable electrochemical behavior, with 93% and 90% of the total capacitance value obtained at 2 $mV.s^{-1}$ for 10 and 16 µm-thick RuN films, respectively, for a 275 s discharge time. Conclusions from **Fig. 3c-d** show impressive capacitance values for RuN electrodes at low and high sweep rates, thus emphasizing the importance of the *F3* family for maximizing both surface capacitance and rate capability [21,39]. The b-coefficient (power law $I_{peak} = a\nu^b$, where *a* and *b* are parameters related to the electrode) was extracted from the CV plots and was consistently measured at ~0.87

± 0.02 (**Fig. S5h**). This result confirms that the charge storage mechanism in the *F3* family electrodes originates from either double layer capacitance or pseudocapacitance[21].

The kinetic limitations of the RuN electrodes were accurately evaluated using electrochemical impedance spectroscopy (**Fig. 3e** and **Fig. S5i**). The Nyquist plots exhibit typical pseudocapacitive behavior, with a semi-circle at high frequency representing the charge transfer process and a quasi-vertical line at low frequency [40]. Bode plots were used to extract the C' and C'' values *vs* frequency to highlight the superior performance of these electrodes. While the C' value at low frequency is similar to that obtained using CV, the frequency curve at which C'' reaches its maximum value *vs* film thickness is more compelling. The time constant ($1/f_{max}$), deduced from these analyses, is plotted *vs* the film thickness in **Fig. 3f**. As expected, it varies from ~1 s (thin RuN layer) to 5 s (16 µm-thick film), reconfirming the impressive rate capability. The graph in **Fig. 3f** shows that both time constant and surface capacitance vary linearly with the film thickness. Lastly, the cycling stability of a 10 µm-thick electrode, evaluated in 1M KOH between -0.4 V and 0.15 V vs Hg/HgO at 50 $mV.s^{-1}$ (**Fig. 3g**), delivers over 95% of its initial capacitance value after 10 000 cycles. The coulombic efficiency of the 10 µm-thick RuN electrode is close to 100 % even after 10 000 cycles in 1M KOH.

To improve the performance, RuN properties were modified through an electrochemical oxidation process (EOP) made in 1M KOH, as described in the supporting information (**Fig. S6a-e**). The CVs of the 550 nm-thick electrodes before and after EOP are presented in **Fig. S6d**, where, post-EOP, the larger butterfly shape clearly demonstrates the superior performance of the modified electrode. The resulting CV is similar to one recently observed for hydrous RuO_2 films in 1M KOH by our group[18]. In this prior study, hydrous RuO_2 was obtained via an electrodeposition process. Thus, the similarity in CV shape suggests that the charge storage mechanism of the modified RuN electrode is strongly correlated to the amount of ruthenium oxide (hydrous or anhydrous) within the film post-EOP. **Figs. S6d-e** show that the surface capacitance, extracted from the CV pre- and post-EOP, doubled at low scan rate. The post-EOP volumetric capacitance reached ~1200 $F.cm^{-3}$ (pre-EOP, C ~ 500 $F.cm^{-3}$). TEM cross-section analyses (**Fig. S6f**) confirm the morphological changes resulting from the EOP. STEM-EELS analyses were carried out at the nanoscale to clarify this modification, and the results are depicted in **Figs. 4a-c**. The **Fig. 4a inset** focuses on two RuN nanofeathers, defining the feather core (red), feather edge (purple) and spacing between them (blue). STEM-EELS was applied at the Ru-$M_{2,3}$ and the O-*K* edges. A close-up STEM-EELS experiment was performed on feather spacing areas to evaluate the presence of oxide in the RuN electrode after the EOP.

Figs. 4b-c present the nanoscale analysis results for the 550 nm-thick RuN electrode pre- and post-EOP. The STEM-EELS image was segmented into three regions (as per the **Fig. 4a inset**), with both the feather edge and the feather core showing similar EELS spectra at Ru $M_{2,3}$-edges and shifted at lower energy compared to RuO_2. Comparing the feather-edge EELS spectra pre- and post-EOP confirms increased oxidation post-EOP (see supplementary information, Discussion on TEM-EELS analyses section). While the Ru M_3 edge maintains the same intensity throughout, the intensity of the O-*K* edge post-EOP is roughly twice that of the pre-EOP RuN film.

The influences of the EOP process on the electrochemical performance of the 10 µm-thick RuN electrode are summarized in **Figs. 4d-f** and **Fig. S6g-k**. Before oxidation (**Fig. 4d)**, the Nyquist plot exhibits typical behavior, with a semi-circle at high frequency representing charge transfer during the pseudocapacitive process, and a near-vertical line characteristic of the electrode's capacitive response. After oxidation (also in **Fig. 4d)**, the shape of the Nyquist plot is modified. While the semi-circle remains present in the high-frequency region, a tilted line with a 45° angle appears at the electrode/electrolyte interface, indicative of a semi-infinite Warburg diffusion process and suggesting that the rate capability of the 10 µm-RuN electrode is affected by the EOP. Bode plots (**Fig. S6g**) reveal that the C' value of the pre-EOP RuN electrode at low frequency is a perfect match for the one evaluated by CV measurements (C' ~ 0.5 $F.cm^{-2}$), and the post-EOP performance of the film is doubled (C' ~ 1.1 $F.cm^{-2}$), reconfirming the benefits of the EOP treatment. The time constant extracted from the C'' vs frequency plot increases from 3.3 to ~10 s for the 10 µm-thick electrodes pre- and post-EOP, respectively, suggesting a moderate impact on the rate capability while retaining a reasonably good performance. The electrochemical performance of the 10 µm-thick electrodes was evaluated by CV in 1M KOH (**Fig. 4e** and **Figs. S6g-k**). The CV at 2 $mV.s^{-1}$ (**Fig. 4e**) shows a change in form, once again shifting from a quasi-rectangular shape to a butterfly one, resulting in a significant increase in area. The surface capacitance values (**Fig. S6h**) extracted from the CVs at 2 $mV.s^{-1}$ change from ~0.45 $F.cm^{-2}$ to ~1 $F.cm^{-2}$, matching those measured by EIS. At 100 $mV.s^{-1}$, the capacitance pre- and post-EOP remains at the same level (~0.3 $F.cm^{-2}$). The cycling stability evaluation of the 10 µm-thick RuN electrode post-EOP (**Fig. 4f**) revealed a capacitance retention of close to 100% after 40 000 cycles in 1M KOH. This suggests that the EOP process significantly boosts capacitance and slightly reduces the rate capability, while the cycling stability remains uncompromised. To the best of our knowledge, this is the first time that this phenomenon occurring between RuN and RuO_2 is reported. At the device level (**fig. S7**), an important factor to evaluate is self-discharge of symmetric and asymmetric configuration, which leads to a drop in cell voltage and a loss of stored energy. **Figure S7k** shows the self-discharge measurement of VN // RuN MSC in 1M KOH during 24 h after fully charging the devices at the maximum cell voltage (1.15 V). From this measurement, we can see that while the RuN electrode maintains a stable potential during 24h (purple plot), the VN electrode potential rises and reaches an equilibrium state close to -0.2 V vs ref after a polarization at -1V vs ref. Therefore, the limiting electrode in the device in regard to self-discharge is the VN electrode.

We investigated the mechanisms involved during the EOP using *operando* X-ray absorption spectroscopy (XAS) [9,41] at the Ru-K edge, along with *ex situ* TEM analyses (**Figs. 5a-c and S8)**. The *operando* XAS allowed real-time observation of the evolution of Ru/RuN and RuO_2 amounts within the 10 µm-thick electrode, by cycling the RuN sample in 1M KOH in a tailor-made XAS cell [9,41] at 2 $mV.s^{-1}$. First, we have compared the Ru K-edge XAS spectra recorded on *ex situ* 10 µm-thick RuN films pre- and post-EOP along with reference materials, such as Ru foil, RuO_2 and hydrous RuO_2 **(Fig. 5a)**. No commercially RuN powder is available as the reference. The XAS spectra of the pristine RuN sample prior to the EOP (green line) closely resembled those of the Ru foil, suggesting a metallic behavior of RuN as previously described. Post-EOP (yellow line), the edge position of the RuN electrode is found between those of the Ru foil and RuO_2 (or hydrous RuO_2) reference materials. To further assess the electrochemical redox reactions, we conducted the *operando* XAS experiment in 1M KOH applying the protocol described in supplementary information (see Operando XAS protocol section). The *operando* XAS measurements (**Fig. 5b**) reveal a shift of the Ru K-edge energy position upon charge/discharge cycling and during the EOP. We assess the Ru (or RuN) *vs* RuO_2 content by using a Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) tool to reconstruct the two principal components and their relative concentrations during cycling, corresponding to 1880 averaged quick-XAS spectra (**Fig. S8c-d**). We also retrieved the information about the chemical species involved in the redox process by a linear combination fitting[42] of the reconstructed principal components along with selected references as Ru, RuO_2 and hydrous RuO_2 (**table 1** in supplementary information file). The relative amount of Ru/RuN and hydrous RuO_2 upon cycling is shown in **Fig. 5c**. It is interesting to note that before soaking the pristine, the 10 µm-thick electrode consists of 88% of Ru/RuN and 12% anhydrous RuO_2, with no hydrous RuO_2 (**Fig. S8e**, **table 1** in SI). The amount of Ru/RuN significantly decreases between ~3000 s and ~8000 s, so during the EOP **(Fig. 5c)**. Concomitantly, the quantity of hydrous RuO_2 increases, as inferred in the standard electrochemical analysis where there is a considerable improvement in the RuN capacitance value post-EOP. Linear Combination Fitting (LCF) results indicate that the post-EOP 10 µm-thick electrode is composed of 80% Ru/RuN and 20% hydrous RuO_2, thereby demonstrating that the EOP involves both oxidation (increase in RuO_2) and hydration processes, as all anhydrous RuO_2 transforms into hydrous RuO_2 post-EOP. TEM analyses (**Fig. S8**) show no change in the nanofeather morphology of the 10 µm-RuN electrode post-EOP, although there is a slight tilt in feather branch. CV measurements pre- and post-EOP (**Fig. 4e**) support this conclusion as the butterfly-shaped CV is typically observed for hydrous RuO_2 in 1M KOH electrolyte [18]. Similar CV characteristics were previously observed in 1990 by S. Trasatti *et al* in 1M KOH [37] for hydrous ruthenium oxide electrodes. Prior to the EOP, the CV of 10 µm-thick RuN film exhibits a box-shape voltammogram, while after the EOP, the redox activities, at ~ 0.1 V and at ~ -

0.4 V vs Hg/HgO, are unambiguously amplified giving rise to a butterfly shape. Considering that the butterfly shape was not observed prior to the EOP, the EOP process plays a key role in the hydration process, as highlighted by the *operando* XAS measurement combined with TEM / EELS analyses. According to the Pourbaix diagram of the ruthenium – H_2O system, at pH = 14 (1M KOH), the electroactive species involved in the redox process are Ru(III), Ru(IV) and Ru(VI). We showed that RuN film is a combination of metallic Ru and RuN phases (the latter constituting the main core of the nanofeather) with amorphous ruthenium oxide localized on the edge of the feather. To understand the role that the nature of the ruthenium oxide has on the electrochemical signature with regard to the butterfly shape, anhydrous ruthenium oxide films were made by magnetron sputtering from a Ru metal target in Ar/O_2 atmosphere (**Fig. S9**). Structural analysis (**Fig. S9a)** confirms, as expected, the formation of a well crystallized film, with the tetragonal phase of RuO_2 (a = 4.52294 Å, c = 3.11333 Å). Electrochemical measurements in 1M KOH were evaluated before and after EOP. The CV signatures of both (box-shape) are similar showing that it is not possible to “boost” the electrochemical performance of already crystallized anhydrous RuO_2 films made by magnetron sputtering (**Fig. S9b-d)**. As a comparison, we have recently[18] demonstrated that amorphous hydrous ruthenium dioxide films made by electrodeposition method clearly exhibit the butterfly-shape CV in 1M KOH (**Fig. S9e-g)**. Consequently, the EOP process seems to boost the electrochemical performance of amorphous ruthenium dioxide due to the hydration process, as highlighted by *operando* XAS.

Finally, it is evident that the RuN film was modified significantly by the oxidation process as the initial operating window potentials were restricted to -0.4 and 0.15 V vs Hg/HgO. Extending this range Pre-EOP would have led to a decrease in cycling stability as a result of unwanted oxidation and reduction reactions. However, post-EOP, it was demonstrated that the suitable electrochemical stability window of the 10 µm-thick RuN film could be extended from -0.8 V to 0.05 V vs Hg/HgO (**Fig. S10)**. The CV plot at 2 mV.s^{-1} is presented in **Fig. 5d**, and the extracted capacitance values at various scan rates (**Fig. 5e**) demonstrate a notable increase in these, leading to ~3.2 F.cm^{-2} (3200 F.cm^{-3}) at 2 mV.s^{-1} and ~0.5 F.cm^{-2} at higher scan rate (100 mV.s^{-1}). Although the rate capability is slightly reduced due to the pre-EOP RuN electrode, the capacitance values obtained still rank among the best for thin film deposition methods. Furthermore, the capacitance retention is also promising, with only minor degradation over 15 000 cycles (**Fig. 5f**).

Pre-EOP, a charge transfer occurs between hydroxide ions (1M KOH) and amorphous RuO_2. For the post-EOP RuN, it involves amorphous hydrous RuO_2. The capacitance of hydrous RuO_2 is higher than that of the anhydrous form [43,44], which explains the significant improvement in volumetric and surface capacitance values post-EOP. Leveraging the large specific surface area of the nanofeather morphology, the high electrical conductivity of the RuN feather core, and the presence of amorphous/hydrous RuO_2 at the feather edge, we have succeeded in developing, for the first time, a high-performance electrode capable of supporting the fast charging process while maintaining high capacitance values and cycling stability. The performance reached by the magnetron sputtered RuN films are compared to state of the art electrode materials based on purely electrosorption, pseudocapacitance or fast charge intercalation process in **Fig. 5g**. For capacitive electrode materials, the time constant τ (in seconds) is a good indicator of its power capability and is calculated as the product of the resistance (**R, ohm**) by the capacitance (**C, Farad**). The current trend is to deliver very high capacitance electrodes at the cost of increased time constants thus significantly reduces the power capability. To minimize time constant, resistance value must be reduced, i.e. at the material level, selecting a material with a high electrical conductivity. Most of the metal nitrides (including RuN) exhibit a metallic-like conductivity. As shown here, the RuN electrode consists of a nanofeather core of RuN with a large surface area. At the edge of the nanofeather electrode, the amorphous hydrous ruthenium dioxide film formed during EOP is responsible for the surface pseudocapacitive charge storage process[45]. The capacitance of RuN electrode is maximized, while its resistance is minimized: the time constant is therefore optimized. Charge (or capacity) is a suitable metric to compare materials with one another. **Fig 5g** shows the evolution of both the volumetric capacity ($Q = C.\Delta V$), in $C.cm^{-3}$ and surface capacity (in $C.cm^{-2}$) vs the time constant, which is a pertinent metric to discuss energy vs power performance at the material level. We observe three sets of electrode materials. In one group, there are carbon-based electrodes (activated carbons, CDC, etc.) and MoS_2 where the charge storage mechanism is governed by purely electrosorption process. The capacitance is not very high, but the main advantage of such carbon-based materials is in the ability to use a large potential window in organic electrolyte, thus enhancing the capacity values. This group of electrode materials is characterized by short time constants (approximately 0.1 up to 1 second) and capacities ranging from 100 to 500 $C.cm^{-3}$. On the other hand, intercalation materials such as Nb_2O_5 are known to exhibit good capacities at the expense of a longer time constant (50 – 100 s) due to lithium-ion diffusion within the electrode. We observe a similar trend with Ti_3C_2 MXene electrodes made from molten salt synthesis and tested in organic electrolyte[46].

In between these two groups are pseudocapacitive materials in aqueous electrolytes. We observe a good compromise between capacities – both volumetric and surface–

and time constant values, showing remarkable performance, for metal nitride electrodes, including the RuN. MnO_2 and $FeWO_4$ materials show low charge values (~ 10-30 $C.cm^{-3}$) in spite of time constants in the range 3 -10 s. Their low electrical conductivity is the main drawback, limiting their power capability. Vanadium nitride is an attractive solution for fast power devices due its good capacity (420 $C.cm^{-3}$) and time constant values (3 – 7 s range). Before EOP, RuN electrodes fit within the same performance range. Similarly, Ti_3C_2 MXene is a class of material possessing both high capacity (500 – 1250 $C.cm^{-3}$) and low time constant (< 10 s) in aqueous electrolyte. With a metallic electrical conductivity, pre-EOP RuN electrodes show very good performance (Q_v ~ 300 $C.cm^{-3}$ and τ ~ 3 s). Post EOP RuN electrodes provides a good compromise between high capacitance (2720 $C.cm^{-3}$ / 2.72 $C.cm^{-2}$) and short time constant (10 s) and, as shown in **Fig. 5g**, is competitive with the best state of the art electrodes.

In summary, we demonstrated that nanofeather RuN film delivers high capacitance (~ 600 $F.cm^{-3}$) with a time constant of less than 6 seconds. An EOP doubles the volumetric capacitance up to 1200 $F.cm^{-3}$, while maintaining excellent cycling stability over 40 000 cycles. *Operando* XAS reveals new insights into the EOP which involves both an oxidation and hydration steps, transforming amorphous anhydrous RuO_2 into hydrous RuO_2. STEM-EELS spectroscopy shows a modification in the feather edge during the oxidation process, while its core, mainly consisting of RuN material, remains unaffected. We were also able to elucidate the charge storage mechanism, demonstrating that the RuN nanofeather electrode benefits from the charge transfer at the electrode/electrolyte interface between the hydroxide ions (from the 1M KOH electrolyte) and the feather-edge amorphous RuO_2 pre-EOP, and the hydrous RuO_2 post-EOP. Furthermore, an extension of the electrochemical window potential from -

0.8 to 0.05 V vs Hg/HgO of post-EOP RuN electrode reveals remarkable performance (3.2 F.cm^{-2} & 3200 F.cm^{-3}), with only a slight decrease in rate capability ($\tau < 10$ seconds). This research establishes that the nanofeather morphology in transition metal nitride films can maximize both capacitance and rate capability of pseudocapacitive electrode for electrochemical capacitors.

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Author Contributions statement

Khac Huy Dinh, Isabelle Roch-Jeune: Methodology, Investigation, Formal analysis, Visualization, Writing – original draft, Writing, Resources, Data curation.

Kevin Robert and David Troadec: Resources.

Houssine Maklouf: Investigations (electrochemical performance in other aqueous electrolytes than 1M KOH)

Antoine Barnabé: Investigation (GDOES)

Marielle Huve, Adrien Teurtrie and Maya Marinova: Formal analysis, Investigation (TEM), Writing – original draft.

Antonella Iadecolla, Camille Douard, Kevin Robert, Christophe Lethien and Thierry Brousse: involved in the design of the XAS cells and the data processing of the XAS spectra, Writing – original draft, review.

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Competing Interest Statement

The authors declare no conflict of interest.

Figure Legends / Captions

Fig. 1 | Schematic of the design and deposition of the nanofeather ruthenium nitride electrode for a micro-supercapacitor: comparison between dense (as observed for instance in $FeWO_4$ film)[34], columnar (as observed for instance in $MnFe_2O_4$ film)[35] and nanofeather RuN film (this work). For all examples, the CV plot was measured in same conditions, at 50 $mV.s^{-1}$ in aqueous electrolyte.

Fig. 2 | Structural and chemical analyses of thin RuN films. a. Transmission Electron Microscope analysis (HAADF images) of a ruthenium nitride electrode, revealing the nanofeather shape of the films. **b.** Diffractogram of the 0.6 µm-thick film showing both cubic Ru metal and RuN phases. **c.** XPS analysis of the RuN film (0.6 µm-thick) from the surface to the RuN/Si_3N_4 interface. **d.** Oxygen and nitrogen depth profiles obtained from GDOES analysis of the RuN Si_3N_4/Si sample.

Fig. 3 | Structural and electrochemical analyses of thick RuN films. a. XRD analysis of various RuN electrodes (0.6, 5, 10 and 16 µm-thick films). **b.** CV plots of ruthenium nitride films at 2 $mV.s^{-1}$ in 1M KOH. **c.** Evolution of the surface capacitance values of RuN electrodes *vs* scan rates in 1M KOH. **d.** Extraction of C_{outer} surface and C_{total} values *vs* film thickness. **e.** Evolution of the C'' and C' values *vs* frequency, from Electrochemical Impedance Spectroscopy of RuN films. **f**. Evolution of the time constant and surface capacitance *vs* film thickness. **g**. Capacitance retention and coulombic efficiency of 10 µm-thick RuN film in 1M KOH at 50 $mV.s^{-1}$.

Fig. 4 | Electrochemical oxidation process on a ruthenium nitride electrode. a. Transmission Electron Microscope analysis of 550 nm-thick RuN film after EOP (electrochemical oxidation process in 1M KOH). The electrode can be described by the assembly of "feather cores" surrounded by "feather edges" and separated by "feather spacings", as shown in the inset. **b-c.** STEM-EELS analysis at the Ru $M_{2,3}$ edges and O-*K* edge of the nanofeather RuN electrode pre- and post-EOP. **d.** Electrochemical Impedance Spectroscopy of 10 µm-thick RuN films before and after the oxidation process. **e.** CV plots of pristine and electrochemically oxidized 10 µm-thick RuN electrodes in 1M KOH at 2 mV.s^{-1}. **f.** Evolution of the capacitance retention in 1M KOH over 40 000 cycles.

Fig. 5 | Investigation of the electrochemical oxidation process (EOP) by (i) *operando* X-Ray Absorption Spectroscopy under synchrotron beam, (ii) TEM analyses, and related electrochemical performance after the oxidation process. **a.** Normalized Ru XANES spectra of the 10 µm-thick RuN electrode (pre-EOP and post-EOP, at 2 mV.s^{-1}) as compared to the Ru foil, RuO_2 and hydrous RuO_2 reference spectrum. **b.** Normalized Ru XANES spectra of the 10 µm-thick RuN electrode acquired during the *operando* measurements in 1M KOH. The inset focuses on the energy shift during the oxidation/reduction process upon cycling and during the EOP. **c.** *Operando* XAS measurement showing the variations in the amount of Ru and RuO_2 species upon charge/discharge cycling (between -0.4 and 0.15 V vs Hg/HgO) and during the EOP (5 CV cycles between -0.4 and 0.5 V vs Hg/HgO at 2 mV.s^{-1}). **d-f.** Post-EOP electrochemical performance evaluation of the 10 µm-thick RuN electrode. **g.** State of the art of the electrode materials including in EC or MSC: evolution of the surface and volumetric capacities vs time constant. Three sets of electrode materials were highlighted depending on the charge storage mechanisms at the electrode / electrolyte interface. The performance of the RuN electrode before and after oxidation are highlighted in these two plots.

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METHODS

Sputtering deposition of RuN thin films

First, to prevent the etching of the standard Si 3-inch double side polished (100) oriented Si substrate by the aqueous electrolyte (1M KOH) used in electrochemical experiments, a high-density layer of Si_3N_4 (300 nm) was deposited onto the both sides of Si wafer using a Low-Pressure Chemical Vapor Deposition technique (LP-CVD) at 800 °C (flow rates : 60 sccm for $NH_{3,}$ and 20 sccm for SiH_2Cl_2, partial pressure : 100mT). The RuN layer was then deposited on the substrate by direct current reactive magnetron sputtering (DC-MS) from a pure 4-inch ruthenium target (99.9%), using a CT200 Alliance Concept reactor under an Ar/N_2 atmosphere. Prior to deposition, the base pressure of the chamber was kept around 4.6 10^{-7} mbar and the target-substrate distance was fixed at 8.5 cm. The sputtering parameters were set as follows: process pressure of 2.0 x 10^{-2} mbar, Ar/N_2 gas ratio of 25/5 sccm, target power density of 0.6 W.cm^{-2} and deposition at room temperature. The deposition and cooling time cycles were adjusted to achieve the desired film thickness and avoid overheating of the target.

Structural and morphological characterizations of the RuN films

Non-contact electrical measurements were conducted using Semilab WT 2000PVN equipment by the eddy-currents method. The morphology of RuN thin film was determined using a Zeiss Ultra 55 Scanning Electron Microscope (SEM) for cross-section and top-view analyses, and a microbalance from Mettler Toledo XP6U was used to establish the density of the films (in g.cm^{-3}).

The structural properties were studied using a 9-kW rotating anode Rigaku SmartLab diffractometer in Bragg-Brentano geometry, delivering Cu Kα radiation (λ= 1.5418 Å).

A 4° offset of the substrate was applied to prevent detector saturation due to the high intensity of the silicon (100) peak. The Raman spectra were collected using the LabRAM HR800 Raman spectrometer (HORIBA Scientific, Jobin-Yvon).

The thin foil extraction was performed by the Focused Ion Beam (FIB) technique with a dual-beam Thermo-Fisher Strata DB235 workstation. The electron beam source was a field emission gun, and a liquid/metal gallium was used for the ion beam source. First, the selected areas were protected with a Pt layer. The extraction was then carried out in two steps: firstly with a beam current of around 10 nA at 15 kV, then with a beam current of approximately 50 pA at 5 kV for the final thinning. This procedure was used in order to minimize amorphization and redeposition, ensuring a homogeneous thickness of the studied regions. The high-angle annular dark field (HAADF) images and STEM-EELS (Scanning Transmission Electron Microscopes - Electron Energy Loss Spectroscopy) observations of thin foils extracted by FIB were performed on a Thermo-Fisher TITAN Themis S/TEM microscope.

Scanning transmission electron microscopy (STEM) analysis was conducted using a high-base Titan Themis 80-300 S/TEM equipped with a high-brightness Schottky field emission gun (X-FEG), a probe aberration corrector and a Wien filter monochromator. This setup was chosen since it provides an optimal spatial resolution of 70 pm, precise electron dose control in non-filtered mode, and a possible energy resolution down to 150 meV in filtered mode. The microscope was also fitted with a direct electron detector (256 x 1024-pixel four-quadrant Medipix) installed behind a GATAN post-column high-resolution energy filter (Quantum ERS/966). In all the electron microscopy experiments, the microscope was operated at 300 kV.

EELS experiments were performed, pre- and post-EOP, on ~0.6 µm-thick FIB lamellas. The monochromated probe was operated with specific settings: an excitation strength of 0.5, a circular C1 aperture in the dispersion plane of 0.5 µm in diameter, a spot size number 9 , and a C3 aperture of 30 µm in diameter. This setting resulted in a probe convergence semi-angle for this configuration was ~15 mrad, and the probe size was ~1 A. The energy resolution for the EELS mode was 300 meV at a dispersion of 0.2 eV/Ch. Under these conditions, the probe current ranged between 70 pA and 100 pA. The collection semi-angle for the EELS signal was 41 mrad with a 5 mm entrance aperture, and for the annular dark-field (ADF) at the entrance of the Gatan imaging filter (GIF), it varied between 41 and 95 mrad. The average t/λ was determined using the log ratio method for 600 nm-thick RuN before and after the electrochemical oxidation process (EOP), leading to lamellas of 0,41 ± 0,1 and 0,39 ± 0,08 respectively. The EELS spectrum images were acquired with sizes of approximately 200 x 60 pixels, a probe step ranging from 0,18 to 0,25 nm per pixel, and a dwell time per pixel of ~50 ms. The analysis of the STEM-EELS data was conducted using the HyperSpy python library [47]. To understand and localize the effect of oxidation on the samples, the data were decomposed into spectra along with their corresponding maps using online robust principal component analysis (ORPCA) [48]. Two thresholds were then set on the first map to spatially segment the spectrum-image into different regions exhibiting similar spectral features.

The Glow Discharge Optical Emission Spectroscopy (GDOES) experiments were carried out using a HORIBA Profiler 2 (650 Pa - 30W) at the Centre de Microcaractérisation Raimond Castaing (Toulouse, France).

The X-ray photoelectron spectroscopy (XPS) experiments were performed using a Kratos Axis Ultra DLD with a monochromatic Al Kα radiation source at Materials

Science and Engineering Department at University of California (Los Angeles, USA). The integrated area of the peaks was found using the CasaXPS software.

Operando X-ray absorption spectroscopy at the Ru K-edge

Synchrotron X-ray absorption spectroscopy (XAS) was carried out on the Ru K-edge in transmission mode at the ROCK beamline [49] of the SOLEIL synchrotron (France). A channel-cut Si(220) quick-XAS monochromator with an oscillating frequency of 2 Hz at the Ru K-edge was used to select the energy of incident photons. Three ionization chambers, filled with a mixture of 20 ml of Ar and 40 ml of N2, were used to monitor incident photons (I0) and the transmitted ones from the sample (I1), along with the RuO_2 reference (I2). A tailor-made three-electrode *in situ/operando* liquid cell was placed between the first and second ionization chambers [41]. A sandwich of Kapton foil (0.01 mm) and PTFE (0.01 mm) served as a transparent window for X-rays, to avoid leaks and prevent beam radiation damage. The *operando* XAS experiment was performed on a 10 µm-thick RuN electrode film deposited on a 400 µm-thick Si substrate and cycled between -0.4 V and +0.15 V vs Hg/HgO at 2 $mV.s^{-1}$, with Pt as the counter electrode. Similarly, the *operando* EOP was performed on a 10 µm-thick RuN film cycled between -0.4 V and +0.5 V vs Hg/HgO at 2 $mV.s^{-1}$. All of the quick-XAS spectra recorded under *operando* conditions were averaged over a period of 10 s to achieve a reasonable signal-to-noise ratio. The Ru foil, RuO_2, and hydrous RuO_2 samples were measured in transmission mode and used as references to assess the Ru oxidation state. The energy calibration and spectra normalization was conducted using a Python graphical user interface (GUI) available at the ROCK beamline [50]. The linear combination fitting was done using the Demeter package [42]. Owing to the high number of spectra obtained (1880 averaged quick-XAS spectra), chemometric analysis was carried out, using a combination of Principal

Component Analysis (PCA) and Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) methods, which are detailed in our previous works[41].

Electrochemical analyses

The electrochemical properties of RuN electrodes were measured in a three-electrode configuration in 1M KOH aqueous electrolyte and in other aqueous electrolytes (0.5M H_2SO_4, 1M LiOH, 1M $LiNO_3$ and 1M Na_2SO_4 see supplementary information file). The RuN films served as the working electrode (WE), a platinum wire as the counter electrode, and either Hg/HgO or Ag/AgCl as the reference electrode depending the selected electrolytes. Cyclic voltammetry (CV), self-discharge measurement and electrochemical impedance spectroscopy (EIS) were carried out on Biologic VMP3 potentiostat/galvanostat equipment. The EIS experiments were performed at open circuit voltage within a frequency range of 100 kHz to 100 mHz, factoring in a 50 mV rms sine-wave voltage amplitude.

The surface capacitance (or ‘areal’ capacitance) measured by CV or galvanostatic charge/discharge (GCD) techniques was calculated by normalizing the capacitance (in mF) according to the tested area (footprint area in cm^{-2}), thereby furnishing real capacitance values in $mF.cm^{-2}$. The specific capacitance (C, $mF.cm^{-2}$), energy density (E, $\mu Wh.cm^{-2}$) and power density (P, $mW.cm^{-2}$) were calculated according to the following equations:

$$C = \frac{\int I dt}{S \Delta V} \quad (1)$$

$$E = \frac{C\,(\Delta V)^2}{2 \times 3.6} \quad (2)$$

$$P = \frac{E}{\Delta t} \tag{3}$$

where I, Δt, S and ΔV are the current (mA), discharge time (second), footprint area (0.407 cm^2) and cell voltage (V), respectively. The volumetric capacitance ($F.cm^{-3}$) was obtained by dividing the areal capacitance by the film thickness, evaluated via SEM in cross sections.

Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.