OPEN ACCESS

Tuning Deposition Conditions for VN Thin Films Electrodes for Microsupercapacitors: Influence of the Substrate Bias Voltage

To cite this article: Allan Lebreton *et al* 2025 *J. Electrochem. Soc.* **172** 040523

Journal of The Electrochemical Society, 2025 **172** 040523

Tuning Deposition Conditions for VN Thin Films Electrodes for Microsupercapacitors: Influence of the Substrate Bias Voltage

Allan Lebreton,[1,2] Christophe Lethien,[2,3,4] Jonathan N. Coleman,[5,z] Thierry Brousse,[1,3,*,z] and Jérémy Barbé[1,2,z]

[1]*Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes, France*
[2]*Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR 3459, 80039 Amiens Cedex, France*
[3]*Institut d'Electronique, de Microélectronique et de Nanotechnologies, Université de Lille, CNRS, Université Polytechnique Hauts-de-France, F-59000 Lille, France*
[4]*Institut Universitaire de France (IUF), 75005 Paris, France*
[5]*School of Physics, CRANN and AMBER Research Centres, Trinity College Dublin, Dublin 2, Ireland*

This study delves into the impact of substrate bias voltage on vanadium nitride thin films deposited via DC magnetron sputtering. By increasing the substrate bias voltage from 0 to −200 V, the microstructure of the films changes from crystalline and porous to amorphous and dense. This obvious change in microstructure is due to atomic peening effect, which is the sputtering of the film by energetic cations at high bias voltage during thin film growth. For capacitive storage devices, it is known that the microstructure of the electrode is key to achieve high capacitance, with the aim to maximize the electrode surface area and concomitantly the areal capacitance, while keeping a low characteristic time to achieve fast charge/discharge rates. In this study, we reveal that a trade-off must be found between areal capacitance and characteristic time. Samples sputtered with low substrate bias voltages present higher areal capacitance but also higher characteristic time compared to thin films sputtered with high substrate bias voltages. The evolution of the characteristic time associated with fast charge/discharge aligns with the electrical conductivity of VN films as determined by four-point probes measurement and indicates that the cycling rate is limited by electrical properties of the VN film.
 [DOI: 10.1149/1945-7111/adc954]

Manuscript submitted January 26, 2025; revised manuscript received March 27, 2025. Published April 22, 2025.

Supplementary material for this article is available online

For almost two decades, vanadium nitride has been studied as potential electrode material for supercapacitors and microsupercapacitors.[1–5] The synthesis of nanosized VN powder is often challenging and difficult to scale up. This is the main reason why most of the research works on VN has been dedicated to the deposition of VN thin films.[6–9] Indeed, VN coatings are commonly used in various domains such as cutting and drilling tools.[10] These coatings are typically deposited by reactive DC sputtering, using a metallic vanadium target and nitrogen as the reactive gas. This deposition method is highly compatible with microelectronics fabrication processes, enabling the production of interdigitated VN-based electrodes for use in microsupercapacitor applications. Besides, the synthesis of a solid-state electrolyte has been developed which enables the fabrication of all solid state microdevices with quite interesting performances.[11]

From a fundamental point of view, the charge storage mechanism of VN has been investigated and the predominant pseudocapacitive charge storage has been evidenced,[4,7,8,12] although at fast charging/discharging regimes the capacitive double layer process brings an additional significant contribution to the overall capacity of the electrodes.

Although our previous studies aimed at investigating the influence of the deposition conditions[9,12] on the electrochemical performances of VN thin film electrodes, advanced deposition techniques were used which will not be compatible with high production rates. For example, reactive high power impulse magnetron sputtering (HiPIMS) was used to improve the corrosion resistance of VN coated steel, but the reported parameters of this technique cannot be compared to our own investigations due to the major differences in the two deposition techniques.[10] Therefore, we have studied more basic sputtering deposition process, using room temperature and standard deposition pressures in order to demonstrate the feasibility of large scale manufacturing processes. Our study aims to emphasize the link between deposition parameters of basic sputtering deposition process and the electrochemical properties of VN thin film electrodes operated in microsupercapacitor device.

As fast charging/discharging regimes are expected for microsupercapacitors similarly to their bulk counterpart, the balance of areal capacitance and characteristic time associated with charge/discharge is a major issue for achieving usable electrodes. Two main parameters have been identified for standard sputtering process, which can be easily adjusted: the bias voltage of the substrate and the thickness of the deposited layer. For clarity purpose, the study of these parameters have been divided in two parts. For each part we use the model developed by Coleman et al. to fit experimental data,[13–16] thus leading to the determination of electrochemical properties such as the maximum capacity of the electrodes and their characteristic time associated with charge/discharge. Although this model has been used for bulk composite electrodes for battery or supercapacitor application, its use for thin film electrode is investigated in the present study. The results provided by the model further helps to propose practical solutions for optimizing VN electrodes in designing microsupercapacitor.

In this part of the study, the analysis of substrate bias voltage effect on the morphology and microstructure of vanadium nitride thin films reveals that atomic peening takes place at high substrate bias voltage values. Atomic peening is the bombardment of the thin film by energetic particles during deposition, which can lead to densification and amorphisation of the thin films. The electrochemical performance in 1 M KOH aqueous electrolytes combined with a semi-empirical fitting model allows to understand the high rate limitations and to find a substrate bias voltage value to reach optimal electrochemical performance regarding both capacity and characteristic time associated with charge/dicharge of the samples.

Materials and Methods

Reactive sputtering.—Sputtering Deposition of VN Thin Film: Prior to the deposition of VN thin films, a highly dense Si_3N_4 layer (300 nm) was deposited by low pressure chemical vapor deposition technique (LP CVD) at 800 °C (flow rates: 60 sccm for NH_3 and

*Electrochemical Society Member.
[z]E-mail: colemaj@tcd.ie; thierry.brousse@univ-nantes.fr; jeremy.barbe@univ-nantes.fr

20 sccm for SiH_2Cl_2) on the top of a silicon wafer in order to prevent the etching of the substrate by KOH (1 M) electrolyte used in electrochemical experiments. VN thin films were deposited by reactive magnetron sputtering (Ar/N_2) from a pure 4 in. vanadium target (99.9%) using an Alliance Concept DP650 reactor. Before the deposition, the pressure was kept below 10^{-6} mbar and the target–substrate distance was fixed at 6 cm. During the thin film deposition, target power, argon and nitrogen flow rates were fixed, respectively, at 150 W, 40 sccm and 2 sccm. In this study, the VN properties were investigated as a function of substrate bias voltage. The substrate was not intentionally heated. Pressure was set at 9.6×10^{-3} mbar during the deposition process. The deposition time was fixed at 31 min in order to obtain samples with thicknesses in the range of 220 nm. Although there is no intentional introduction of molecular O_2 in the reactor, films contain a significant fraction of oxygen, which is explained by oxidation during exposure to air, due to the high getter property of vanadium and porosity of the films. This is why the obtained VN thin films also contain a significant fraction of amorphous vanadium oxide. Our results suggest that the films are composed of two distinct phases: vanadium nitride in the bulk and vanadium oxides at the surface.[17]

Thin film characterization.—Room temperature XRD data were obtained using a Bruker "D8 Advance" diffractometer operated in Bragg-Brentano geometry with a Cu anode sealed X-ray tube and a focusing Ge(111) primary monochromator (selecting the Cu Kα1 radiation; $\lambda = 1.540598$ Å). We used a 1-D silicon-strip position sensitive detector ("LynxEye" detector) with an active area of 3.7° 2Θ (goniometer radius: 217.5 mm).

SEM measurements were conducted on a ZEISS Merlin instrument, in secondary electron configuration.

XPS measurements were conducted on a Kratos Axis Ultra Instrument, using a monochromated Al Kα source (1486.6 eV) operating at 225 W. Wide range spectra were realised prior to core level measurements of the different elements detected with pass energy of 80 eV. The pass energy and the step scan to measure the region of interest were fixed to 40 eV and 0.1 eV, respectively. The typical probed depth was 10 nm over a 700×300 μm^2 zone. The dwell time and number of sweeps were chosen such as the highest XPS peak of the selected zone exhibits, at least, 100 000 counts. Charge neutralization was used when acquiring the spectra. The energy calibration was set from C1s signal allotted to adventitious carbon (C–C bonds) fixed at 284.9 eV. Using CasaXPS software,[18] the elemental composition was determined from the area under C1s, O1s, V2p and N1s peaks after removal of a Shirley-type background.

Conductivity measurement were performed by four-points probe method using a pro4 device from Lucas Labs connected with a Keithley 2601 A system source-meter. The software used to run those experiments was Pro4 and the measurements were performed applying a current of 10 mA with a 5% tolerance.

The topography of the samples was characterized in air using a Nanowizard II atomic force microscope (AFM) (JPK Instruments, Berlin, Germany) operating in the intermittent contact mode. Tips used were made of silicon (PPP-NCHR, Nanosensors).

Electrochemical measurements.—Aqueous electrochemical measurements were performed in 1 M KOH aqueous electrolyte using three electrode cell. Hg/HgO was used as reference electrode and a platinum wire as the counter electrode. Nitrogen bubbling was carried out prior to measurement to eliminate dissolved O_2 from the electrolyte. The potential window was fixed between −1 V and −0.4 V vs Hg/HgO reference electrode to avoid any side reaction and/or additional sample degradation.[19]

Organic medium electrochemical measurements were performed in 0.1 M Tetraethylammonium tetrafluoroborate (TEATFB) in acetonitrile (ACN) electrolyte under air atmosphere using three-electrode cell. Silver wire was used as quasi-reference electrode (QRE) and a platinum wire as the counter electrode. The potential window was fixed between −0.7 V and 0.2 V vs silver quasi-reference electrode to avoid any side reaction and/or additional sample degradation.

VMP3 potentiostat/galvanostat (Biologic) monitored by EC-lab software, was used for data collection and data treatment. The protocol to analyse the electrochemical properties was the same for all samples: (i) 50 activation cycles at 20 $mV.s^{-1}$ were performed before measurements. (ii) CV measurements were realised with scan rates ranging from 5 to 10 000 $mV.s^{-1}$ in aqueous media and from 10 to 10 000 $mV.s^{-1}$ in organic media. All measurements were conducted at a temperature of 295 K.

Electrochemical impedance spectroscopy (EIS) measurements were performed with a AC signal with an amplitude of 10 mV between 100 mHz and 1 MHz at open circuit voltage (OCV).

Results and Discussion

In this study, the effect of substrate bias voltage during vanadium nitride thin film deposition using DC magnetron sputtering process was investigated. Substrate bias voltage was varied from 0 V to −200 V. For ease of understanding, the term "increase" of substrate bias voltage is used to depict the increase in absolute value from 0 to −200 V.

Top-view and cross-section SEM images of vanadium nitride thin films deposited with increasing substrate bias voltages are presented in Fig. 1. Columnar growth typical of sputtering deposition process is observed for all samples (Figs. 1(f)–(j)).[3,4,7,9,10,20] At the surface, 30–40 nm-large pyramids representative of the top of the columns are seen for samples sputtered with bias voltages of 0 V and −50 V (Fig. 1a, 1b). Those morphologies are expected for low values of bias voltages, as described by Lethien et al.[3,4,7,9,10,20,21] However, when bias voltage exceeds −100 V (Figs. 1c–1e), the surface morphology gradually flattens and shifts to a cauliflower-like structure[17,21] typically observed after a densification process.

Atomic force microscopy measurements were performed in order to get information on the surface morphology of the thin films. For the samples sputtered at 0 V and −50 V (Figs. 1k and l), one can observe the pyramidal microstructure previously described. Pyramid dimensions of 30–40 nm correspond to those measured by top-view SEM analysis. A high RMS (root mean square) roughness of 2.4 nm is measured. When the bias voltage is increased (from −100 V to −200 V), we observe a clear decrease of the RMS roughness to 1.1 nm, which agrees with a "flattening" and a shift to a cauliflower-like structure.

This change in microstructure from a pyramidal to a cauliflower-like surface morphology when substrate bias voltage is increased can be explained by so-called atomic peening effect, which is described in Fig. 2.[22,23] With the increased negative bias voltage on the substrate, the kinetic energy of sputtered metal cations and argon cations is increased in the direction of the substrate. At high bias voltage values, ions arriving on the substrate/film with high energy can sputter in turn the growing film. Thus, there is a trade-off between deposition (of neutral species mostly) and re-sputtering (by cations), which directly impacts the microstructure. It generally induces a densification of the microstructure and a decrease in the crystallinity as compared to films grown at low bias voltage values, for which the atomic peening effect is negligible. This densification may also be explained by higher energy brought to the film by energetic cations, which increases atoms surface diffusion, as for HiPIMS (High Power Impulse magnetron sputtering) processes.[24] Figure 2b indicates a small decrease of thickness mean value, from 255 nm to 215 nm (corresponding to deposition rates from 8.2 $nm.min^{-1}$ to 6.9 $nm.min^{-1}$) when the bias voltage increases from 0 V to −200 V. This decrease of film thickness is in line with a densification of the film.

The in-plane electronic conductivity of the samples was measured using four-points-probe method. Results are presented in Fig. 2c. A clear increase in conductivity with substrate bias voltage is observed. The conductivity increases from 1876 $S.cm^{-1}$ to 5341 $S.cm^{-1}$, almost three times higher, when bias voltage increases from 0 V to −200 V.

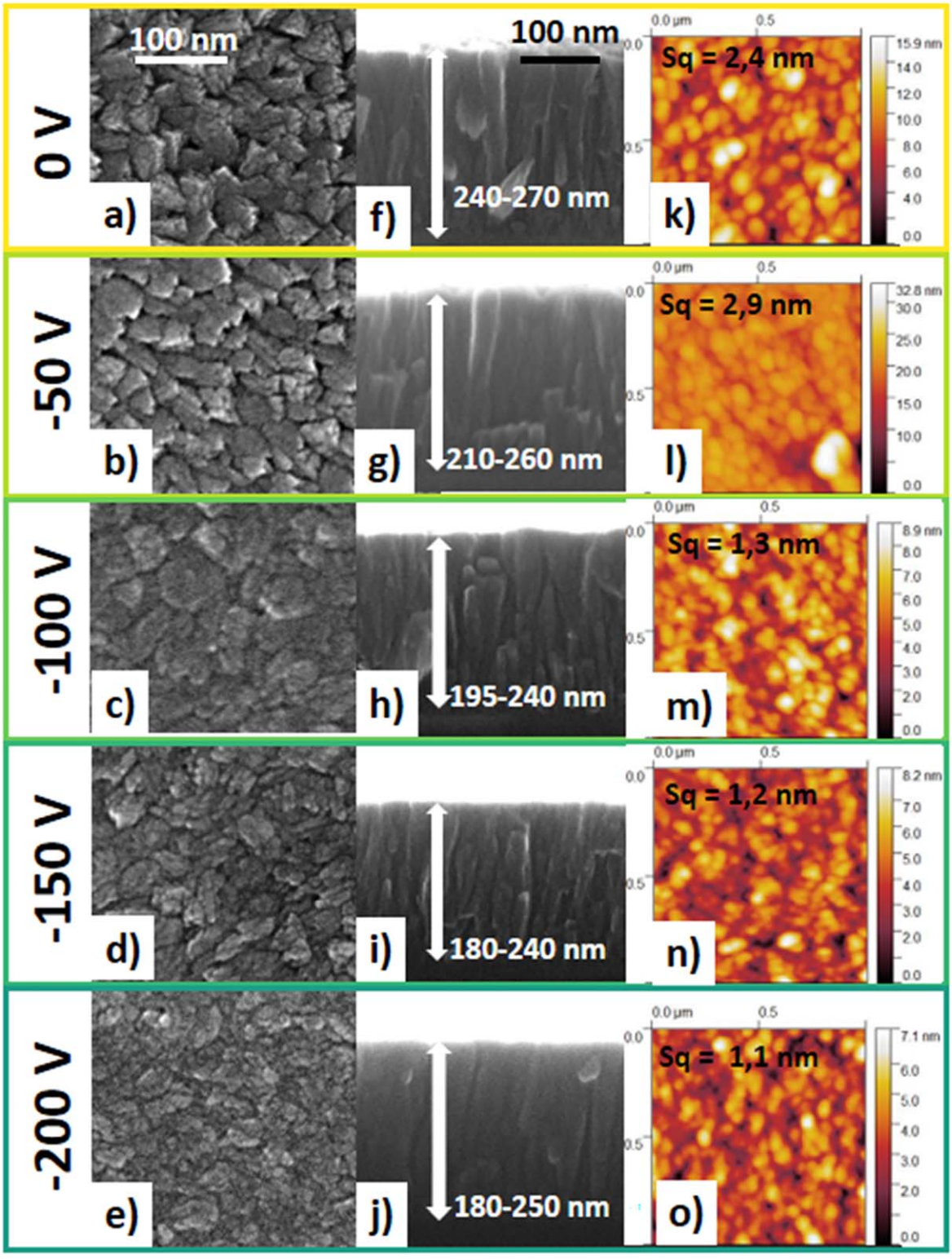

Figure 1. (a)–(e) SEM top-view and (f)–(j) cross section images and (k)–(o) AFM scans images of vanadium nitride thin films sputtered for 31 min with bias voltage ranging from 0 V to −200 V.

These results are explained by thin film densification. Indeed, the in-plane conductivity is highly dependent on the tortuosity of the films and the inter-columnar spacing. As the film density increases with bias voltage, the inter-columnar spacing decreases, which facilitates the transport of charges in the in-plane direction. We note that the highest value obtained (5341 $S.cm^{-1}$) remain lower than bulk vanadium nitride conductivity (1.6×10^4 $S.cm^{-1}$),[25] which is explained by the columnar structure of the film, but is higher than most values reported in literature for vanadium nitride thin films.[9] This shows the benefit of polarizing the substrate to maximize the electrical performance of VN films.

XRD measurements were performed in the 10° to 80° 2Θ range. All thin films present a preferential (111) orientation at 37.5° and no other diffraction peaks were observed. A decrease of (111) peak

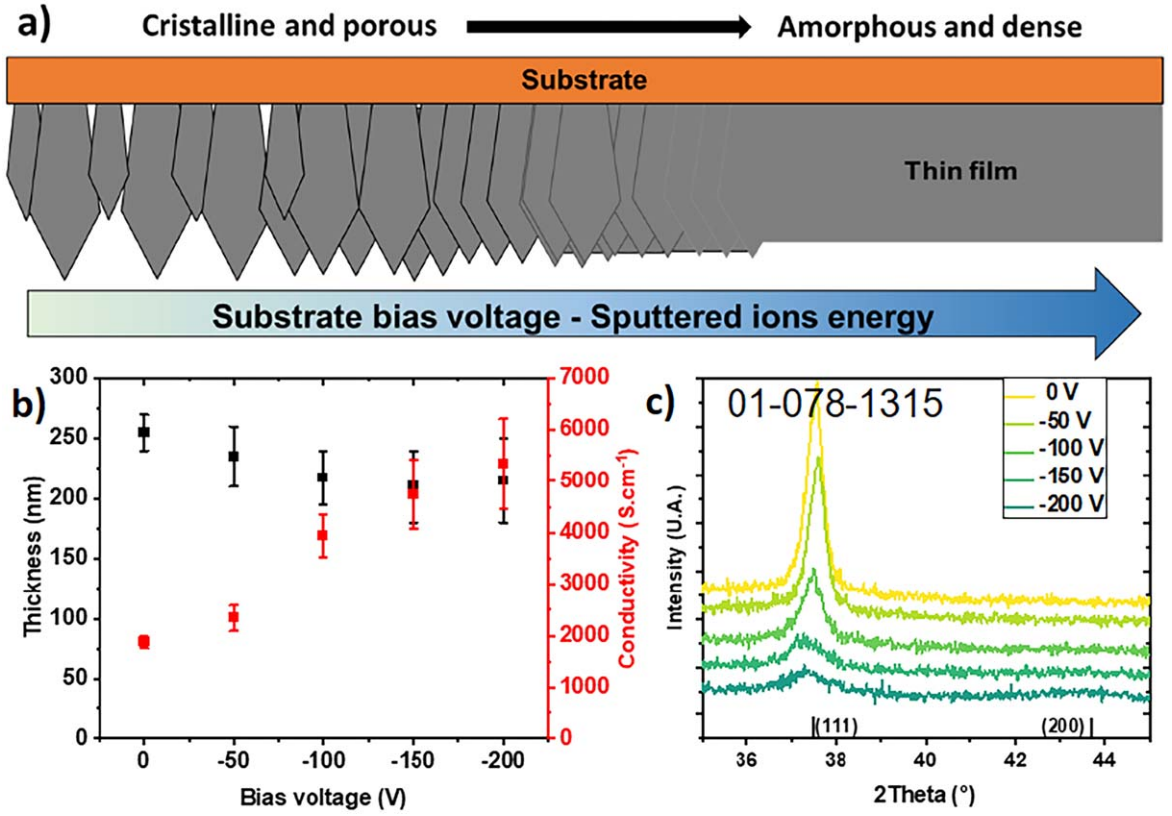

Figure 2. (a) Atomic peening effect occurring during a sputtering deposition process (b) plot representing thickness and in plane conductivity vs substrate bias voltage. (c) X-ray diffractograms of vanadium nitride thin films sputtered with bias voltage ranging from 0 V to −200 V.

intensity is observed in combination with an increase of FWHM when bias voltage increases. Those two observations clearly indicate an amorphization and decrease of grain size of vanadium nitride thin films when bias voltage increases. Similarly to the SEM and AFM results, the analysis of the samples can be divided into two groups: low bias voltages (0 V and −50 V) and high bias voltages (from −100 V to −200 V), with the former clearly showing higher crystallinity than the latter.

XPS measurements were performed in order to get information on the surface thin films composition as well as to determine the oxidation states of vanadium. Figure 3a shows the survey scan of the sample sputtered without substrate bias voltage. Four elements were detected: oxygen, vanadium, nitrogen and carbon. No oxygen or carbon was intentionally introduced in the reactor during deposition. The presence of these two elements in the films is due to residual oxygen in the reactor as well as air exposure before introduction in the XPS chamber as discussed before. The evolution of thin film composition vs substrate bias voltage is presented in Fig. 3b. In agreement with previous results, we observe two groups of samples at low bias voltages (0 V and −50 V) and high bias voltages (from −100 V to −200 V), presenting distinct compositions. The vanadium and carbon contents remain stable with bias voltage, both around 25%, whereas nitrogen content increases from 28% to 32%, and oxygen content decreases from 20% to 16% with increasing substrate bias voltage. The decrease in oxygen content is in agreement with the film densification as oxygen diffusion within the VN films is significantly hindered in dense layers.

The deconvolution of the V2p3/2 region is represented in Fig. 3c. This deconvolution follows the work made by Biesinger et al.[26,27] and is based on four different components related to the oxidation states of vanadium in VN, V_2O_3, VO_2 and V_2O_5. They are respectively located at binding energies of 513.7 eV, 514.3 eV 515.85 eV and 517.2 eV.[18,26,27] Based on this decomposition, the evolution of the different components with substrate bias voltage is presented in Figs. 3d, 3e. Clearly, vanadium with low oxidation states tend to increase at the expense of vanadium with high oxidation states, when substrate bias voltage increases. The VN component slightly increases (from 20–21% to 25–26%) with increasing bias, whereas the V_2O_5 component decreases from 31–32% to 26–27%. The VO_2 and V_2O_3 components (fitted as one component with higher FWHM) remain stable around 48% together. From previous results, the vanadium oxidation degrees expected to be involved in the Faradaic reactions are V^{+III} and V^{+IV}.[10] Here, two groups of samples are observed with more VN and less V_2O_5 (V^{+V}) present at high substrate polarisations, whereas the V^{+III} and V^{+IV} oxides appear to remain unchanged. These findings are consistent with our previous study in the field using TEM-EELS analytical tools for comparison purpose with XPS data.[12]

In pseudocapacitive materials such as vanadium nitride, charges can be stored through three different processes. First, by Faradaic fast redox reactions taking place at the surface or near surface of the electrode involving H^+ insertion through a thin layer below the surface of the material, which is the Faradaic part. This mechanism should result in a pair of redox peaks in the cyclic voltammograms. Second, by purely capacitive electrochemical double layer capacitance (EDLC). EDLC is directly dependent on the electrode specific surface area. Third, by pseudocapacitive behaviour implying a delocalization of redox potentials over the whole potential window, as shown recently by O. Fontaine et al.[28] These last two mechanisms should lead to a box-type shape CV. One way to qualitatively compare the specific surface area of vanadium nitride thin films is by comparing their Electrochemical Double-Layer Capacitance (EDLC) values, which can be assessed by cycling the thin film electrodes in an organic electrolyte. Indeed, the lack of water molecules inhibits the charge transfer at the electrode/electrolyte interface. As VN is electronically conductive, only double layer capacitance is observed. Subsequently, this cycling process in organic media effectively eliminates both faradic and pseudocapacitive

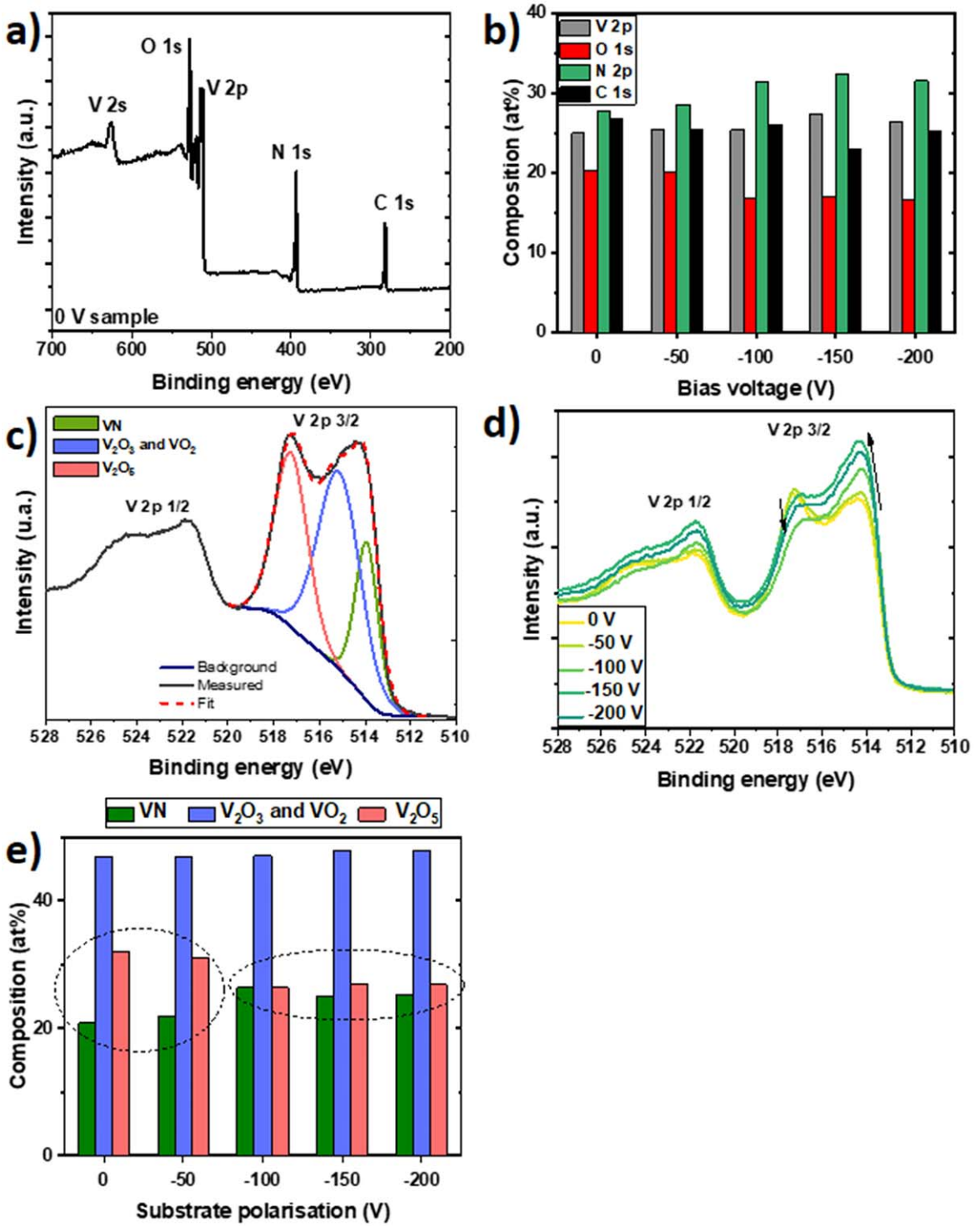

Figure 3. (a) Wide scan XPS spectrum of the VN thin film sputtered without substrate bias voltage (0 V). (b) Compositions of VN thin films measured by XPS. (c) Deconvolution example of vanadium 2p3/2 region for the sample sputtered without bias voltage. (d) V2p core level of VN thin films sputtered at different substrate bias voltages. (e) Results of the deconvolution of VN 2p3/2.

contributions. Vanadium nitride thin films were cycled in 0.1 M tetraethylammonium tetrafluoroborate (TEATFB) in acetonitrile (ACN), at scan rates ranging from 10 $mV.s^{-1}$ to 10 000 $mV.s^{-1}$. Cyclic voltammograms (CV) measured at scan rate of 10 $mV.s^{-1}$s are presented in Fig. 4a for various substrate bias voltages. We can identify side reactions (water dissociation due to air exposure of the system during cycling) taking place at potentials lower than −0.5 V vs Ag QRE (quasi reference electrode). For higher potentials, we can observe a rectangular shape voltammogram typically observed for capacitive or pseudocapacitive materials. However, as regard to the low values of current and capacitance measured here, it is believed that the VN films tested in organic electrolyte exhibit only pure EDLC without pseudocapacitance. Similar observations were made by Jrondi et al. on sputtered VN films[4] in ionic liquids. The areal capacitance (EDLC) vs scan rate is presented in Fig. 4b. The thin film electrodes prepared at high bias voltages (−100 to −200 V) exhibit very low capacitance regardless of the scan rate. In contrast, the electrodes prepared at low bias voltages (0 and −50 V) show

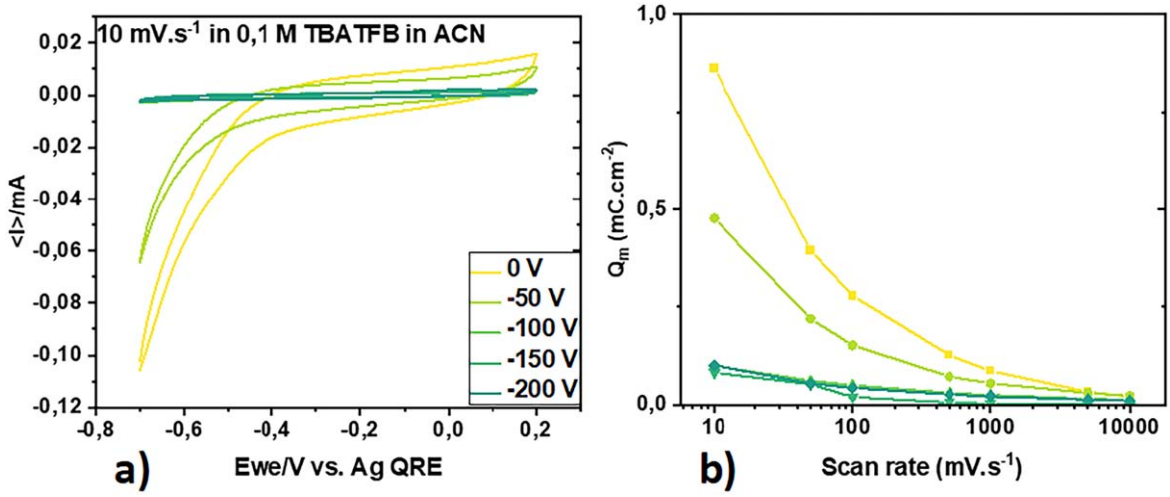

Figure 4. (a) Cyclic voltammograms at 10 mV.s^{-1} in 0.1 M TEATFB in ACN and (b) areal charge vs scan rate of vanadium nitride thin films sputtered with different substrate bias voltages.

significantly higher capacitance at low scan rates, which decreases rapidly as the scan rate increases. Since the EDLC charge is directly proportional to the surface area, this supports the hypothesis of growing denser films with lower surface area when applying high bias voltages during sputtering.

The aforementioned observations, i.e. change in microstructure (SEM, AFM and XRD), decreased thickness, increased electrical conductivity, decrease of surface oxygen content and decrease of EDLC capacitance with increasing substrate bias voltage are all highlighting a densification and amorphization of the thin films due to atomic peening at bias voltages higher than −100 V.

The next part of this paper will focus on the influence of atomic peening on electrochemical behaviour of vanadium nitride thin films. The electrochemical performance of sputtered VN films with different substrate bias voltages will be discussed based on cyclic voltammetry and impedance spectroscopy carried out in 1 M KOH in order to get information about the rate capability of the VN electrodes. A simple model will be used to fit capacity-rate curves and extract the characteristic time (τ) associated with charge/discharge processes.

Figure 5a–5d show the cyclic voltammetry of VN films in 1 M KOH from 5 mV.s^{-1} to 10 000 mV.s^{-1}. Rectangular CV shapes combined with a redox peak around −0.65 V vs Hg/HgO typical of vanadium nitride are observed at 10 mV.s^{-1} in Fig. 5a. The box-type shape envelope has been assigned to capacitive and pseudocapacitive charge storage, while the pair of redox peaks depict intercalation of ions from the electrolyte in a thin layer at the surface of the particles, leading to an electron transfer and a subsequent change in vanadium oxidation state. It is clear that at low scan rate, the intensity of the current decreases when substrate bias voltage increases (as indicated by the black arrows), although the film thickness does not significantly vary with the substrate bias voltage. Samples deposited at 0 V and −50 V present comparable performance.

At 100 mV.s^{-1} (Fig. 5b), the same CV shape is observed but the reduction and oxidation peaks present a shift which is particularly large at low bias voltage values (0 V and −50 V). This mismatch between oxidation and reduction peaks potentials indicates lower reversibility,[29] suggesting that films prepared at high substrate bias voltage would have higher reversibility. Samples sputtered with low bias voltage are however still providing the largest CV areas, i.e. capacity.

If the scan rate is further increased to 1000 mV.s^{-1}, a switch from capacitive/pseudocapacitive to resistive behaviour is observed for samples sputtered at 0 V and −50 V (Fig. 5c). Samples sputtered at −100 V and −150 V show an intermediate behaviour while the sample sputtered at −200 V is the only one still providing a fully pseudocapacitive behaviour at 1000 mV.s^{-1}, probably due to the higher electrical conductivity of the sample made at −200 V (see Fig. 2b). Samples providing the largest CV areas are then the ones sputtered at −100 V and −150 V. It seems that when substrate bias voltage increases, the reversibility at high scan rate increases too, which is consistent with the conductivity measurements presented in Fig. 2b.

Last, Fig. 5d presents the cyclic voltammograms at 10 000 mV.s^{-1}. It clearly shows that all the samples are resistive at this scan rate, except the one sputtered at −200 V which still present an intermediate behaviour. This sample is the only one able to store some charge at this scan rate, although the capacity is low.

The areal charge vs scan rate has been extracted from the CVs and is presented in Fig. 6a. We observe that samples sputtered with low substrate bias voltage (0 V and −50 V) provide higher charge at low scan rate but lower charge at high scan rate, as compared to samples sputtered with high substrate bias voltage. The highest areal charge is obtained with the sample sputtered at 0 V, presenting 8.93 mC.cm^{-2} corresponding to 14.9 mF.cm^{-2} or 583 F.cm^{-3} at 5 mV.s^{-1}.

Even though the charge at high scan rates is rarely presented, it can provide interesting information about the characteristic time associated with charge/discharge of the thin film. The evolution of the contribution of pure EDLC capacitance to the total capacitance determined from measurements in organic electrolyte and aqueous electrolyte is presented in Fig. 6b at different scan rates. It highlights the very limited contribution of double layer capacitance (EDLC) at low scan rates, never exceeding 15% of the total charge, thus evidencing the importance of pseudocapacitive processes at low scan rates.[28] However, the EDLC contribution increases drastically at high scan rates for the electrodes deposited with 0 and −50 V bias voltage. This observation can be explained by the absence of any redox peak for samples sputtered at 0 V and −50 V from 1000 mV.s^{-1}. Indeed, faradaic reactions are supposed to be slower than double layer capacitance or pseudocapacitance, which is in agreement with the observations.

Electrochemical impedance measurements were performed and the resulting Nyquist plots are represented in Fig. 7a for all substrate bias. We can clearly identify a decrease of film resistance as the Nyquist plots shift to the left when substrate bias increases. Evolution of the resistance and the CPE constant obtained using Zfit application in EC-Lab software with a R-CPE circuit in parallel configuration are represented in Figs. 7b and 7c. We can identify the decrease of the resistance with substrate bias, which is expected due to the film densification identified previously. A decrease in the CPE

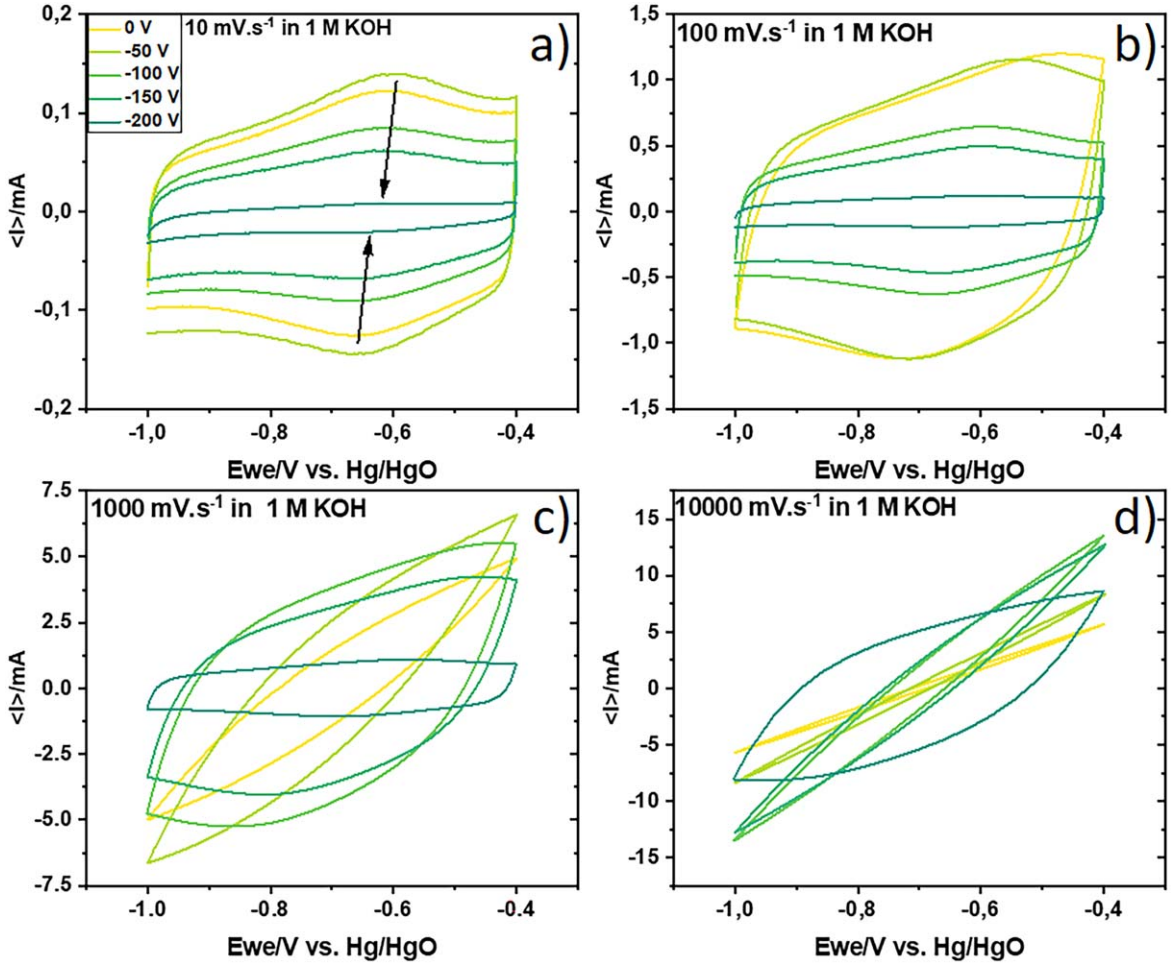

Figure 5. (a)–(d) Cyclic voltammograms of vanadium nitride thin films sputtered with different substrate bias voltages measured in 1 M KOH at scan rates of respectively, 10 mV.s^{-1}, 100 mV.s^{-1}, 1000 mV.s^{-1} and 10 000 mV.s^{-1}.

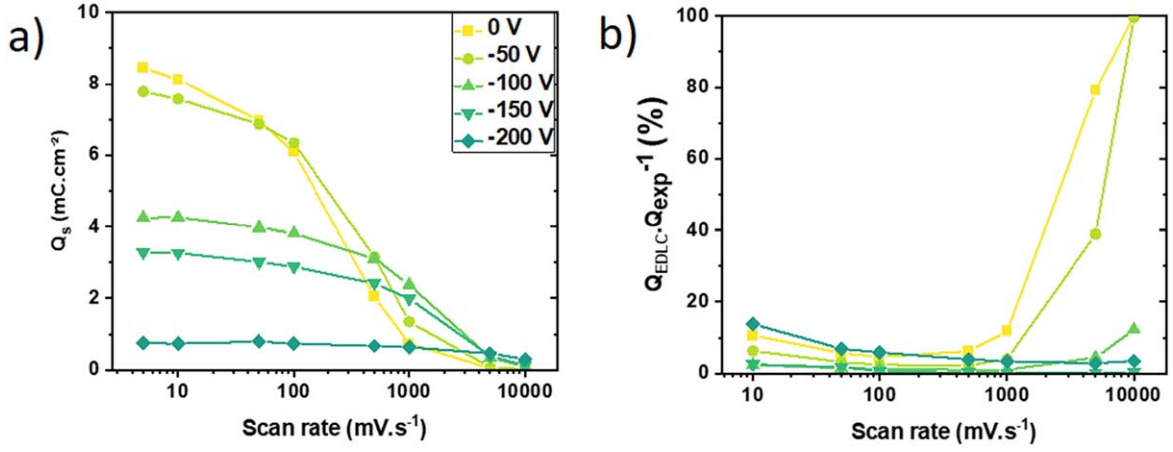

Figure 6. (a) Evolution of the areal charge Q_s vs scan rate and (b) evolution of the ratio between charge in organic electrolyte and charge in aqueous electrolyte vs scan rate of vanadium nitride thin films sputtered at different substrate bias voltage.

constant for the electrodes deposited at high bias voltage, which indicates a reduction in the charge stored, is also observed.

The conductivities obtained using four-point probe measurement and electrochemical impedance measurement are compared in Fig. 7d. It appears that the conductivity obtained using the four-point probe measurement is more than two times higher than the value obtained with electrochemical impedance spectroscopy.

The characteristic time associated with charge/discharge process, τ, represents the transition from capacitive/pseudocapacitive to resistive behaviour.[30] Estimating this value using CV shapes is inappropriate due to the indistinct boundary between rectangular and resistive shapes, leading to subjective determinations. To overcome this challenge and obtain a clear determination of τ, models have been developed utilizing electrochemical impedance spectroscopy

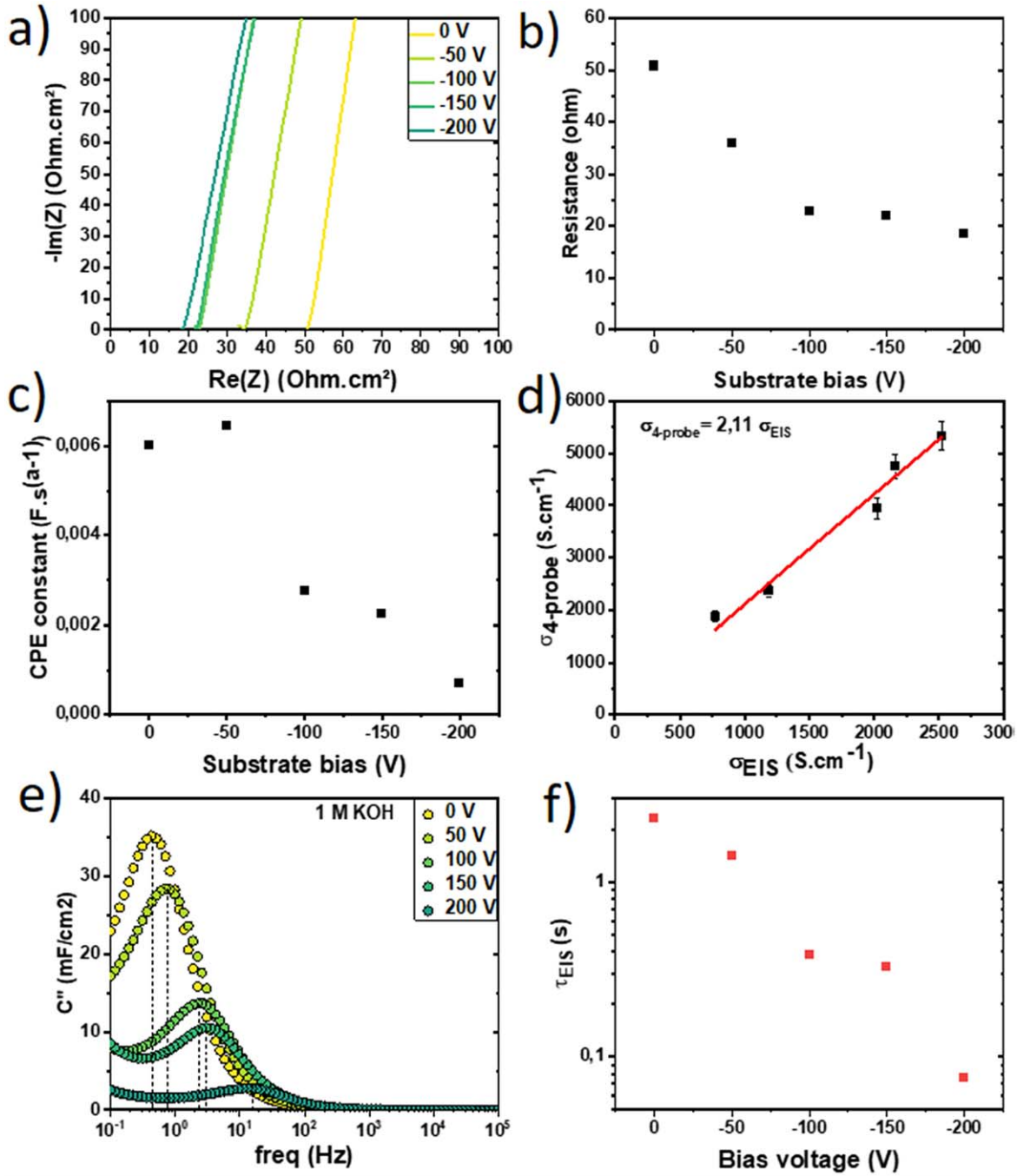

Figure 7. (a) Evolution of the areal charge Q_s vs scan rate and (b) evolution of the ratio between charge in organic electrolyte and charge in aqueous electrolyte vs scan rate of vanadium nitride thin films sputtered at different substrate bias voltage. (c) Representation of imaginary and real part of capacitance C (ω), respectively C' (ω) and C' (ω) vs frequency in EIS. (d) Characteristic times associated with charge/discharge τEIS vs substrate bias voltage.

data or charge vs scan rate plots.[16–20] The subsequent section will detail both of these models. τ_{EIS} will be used to describe the characteristic time associated with charge/discharge calculated using electrochemical impedance spectroscopy and τ_{fit} the characteristic time associated with charge/discharge calculated using the fit of charge vs scan rate plots.

Impedance spectroscopy has been carried out to extract the characteristic time associated with charge/discharge τ_{EIS}. Figure 7e represents the evolution of C′ vs frequency. This value represents the imaginary part of the capacitance C(ω), defined by Eq. 1 with Z(ω) being the complex impedance, Z′(ω) the real part of impedance and ω the frequency. On this graph, the characteristic time associated with charge/discharge τ_{EIS} corresponds to the opposite of the frequency determined at the maximum C′ value.

$$C''(\omega) = \frac{-Z'(\omega)}{\omega\,|Z(\omega)|^2} \qquad [1]$$

Characteristic times associated with charge/discharge τ_{EIS} obtained using this method vs substrate bias voltage are represented in Fig. 7f. A decrease from 2.3 s to 0.076 s is observed when bias voltage increases. These values are in perfect agreement with the characteristic times associated with charge/discharge observed for pseudocapacitive material tested in aqueous electrolyte.[31] This decrease of the characteristic time associated with charge/discharge with increasing bias voltage means that samples prepared with high

bias voltage can be charged or discharged faster without major drop in capacitance. This is most probably explained by the higher electronic conductivity of the VN thin films deposited at high substrate bias voltages, as well as less porous/tortuous films, both of them due to atomic peening process resulting from the sample bias voltage during the sputtering process.

Next, we have used a fitting model developed recently[13–16] to determine directly and simultaneously the maximum capacity, characteristic time associated with charge/discharge and capacity decay slope at high cycling rate for each sample. This method consists principally in fitting the capacity vs scan rate plots, using Eq. 2. In this equation, Q_{exp} corresponds to the measured charge, Q_m to the maximum charge at low scan rates and R to the rate in cycle.h^{-1}. τ_{fit} is the characteristic time associated with charge/discharge of the sample in h.cycle^{-1} and finally n is the power law decay at high cycling rates.

$$Q_{\text{exp}} = Q_m[1 - (R\tau_{fit})^n(e^{-(R\tau_{fit})^{-n}})] \;\; with \;\; R = \frac{I}{Q_{\text{exp}}} \qquad [2]$$

The results are displayed in Fig. 8a and all plots present very good fit ($R^2 > 0.99$). The maximum capacity Q_m is presented in Fig. 8b. One can observe a very slight decrease between the samples sputtered at 0 V and −50 V (from 12.5 mC.cm^{-2} to 12 mC.cm^{-2}) followed by a sharp decrease of maximum capacity until −200 V. This decrease can be explained by various factors, such as sample densification, which results in less accessible specific surface area. The smaller proportion of vanadium oxides on the surface (Fig. 5b) with increasing bias voltages can also explain the reduced capacity as surface vanadium oxide phases are responsible for the faradaic storage. Based on recent studies, a trade-off exists between high capacity and cycling stability in V_2O_5. High proportions of V_2O_5 on the film's surface increase capacity but reduce cycling stability due to vanadium oxide dissolution in the electrolyte (V^{5+} as VO_4^{3-} ions), followed by vanadium nitride dissolution and delamination. Adding vanadate ions to the electrolyte beforehand can prevent vanadium dissolution from the electrode.[32]

The evolution of the n parameter is shown in Fig. 8c. Values are very close to 1 for bias voltage values between 0 V and −150 V. It was previously described that the n value should be close to 0.5 for diffusion limited systems and 1 for resistance limited systems.[13–16] This indicates that for all of those samples the factor limiting the high-rate cycling would be the electrode electronic conductivity. For the sample sputtered with a substrate bias voltage of −200 V (dark green), the fitting was performed with n value forced to 1 as there are not enough data points to fit properly the data. The goodness of fit R^2 determined with n fixed to 1, or not fixed (fitted) is very similar in both cases, as shown in SI.

The evolution of the characteristic times associated with charge/discharge τ_{EIS} and τ_{fit} vs bias voltage is presented in Fig. 8d. Even though those two values are calculated using respectively EIS measurements or the fitting model based on Eq. 2, they are both

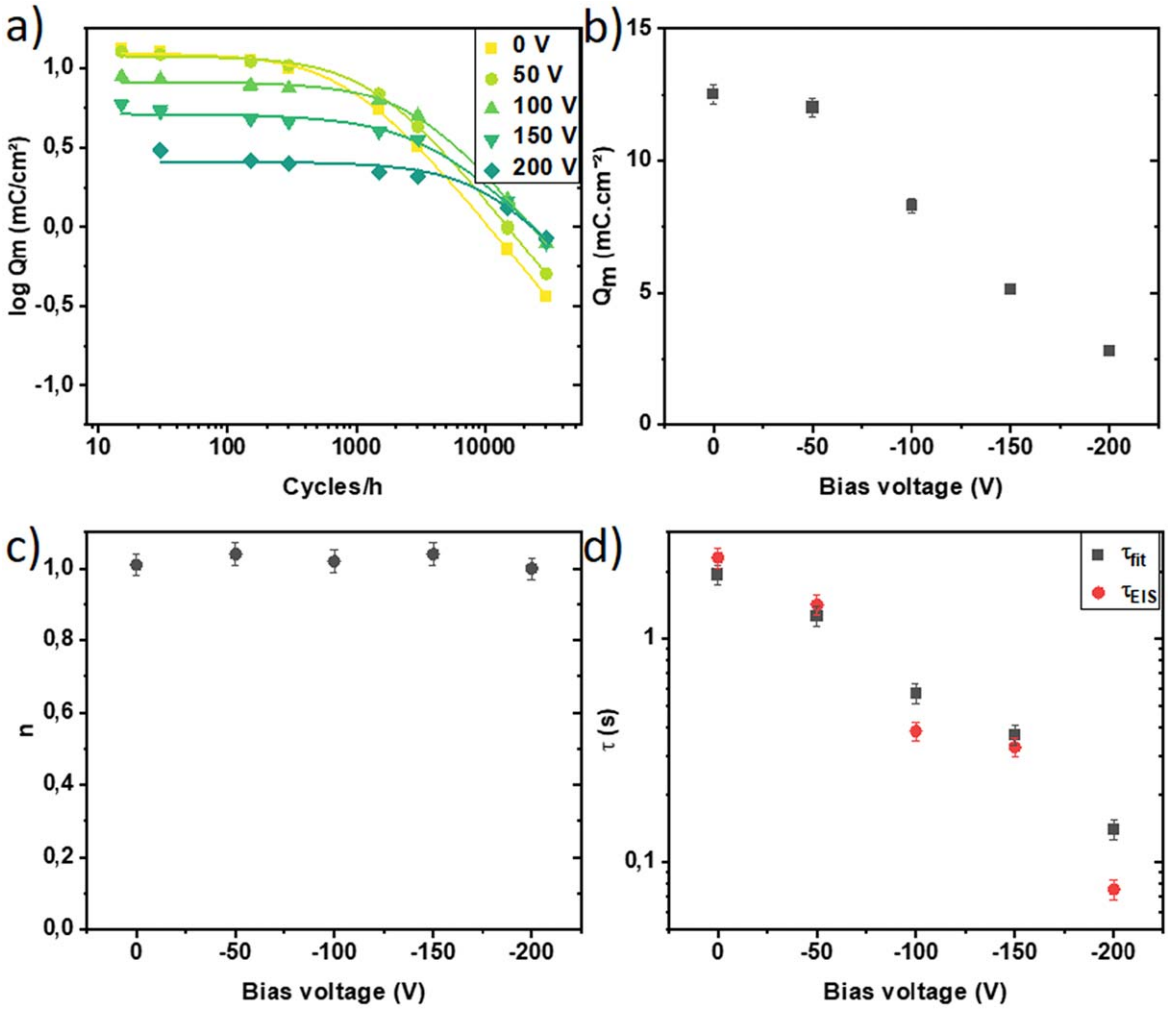

Figure 8. (a) areal charge vs scan rate of vanadium nitride thin films sputtered at various substrate bias voltages cycled in 1 M KOH. Curves are fitted using Eq. 3. (b) Evolution of maximum charge Q_m vs substrate bias voltage. (c) Evolution of n value vs substrate bias voltage. (d) Evolution of the characteristic times associated with charge/discharge determined by EIS (in red) and fit (in black) vs substrate bias voltage.

describing the time at which the sample presents a switch from capacitive/pseudocapacitive to resistive behaviour. Both methods result in comparable characteristic times associated with charge/discharge. The overall trend evidences the decrease of characteristic time associated with charge/discharge with increasing bias voltage. As described previously, this decrease can be related to the VN electrode conductivity, which is also related to its microstructure and composition.

It appears that the semi-empiric model used is well fitted to describe the electrochemical behaviour of pseudocapacitive vanadium nitride thin films. To assess the accuracy of the charge/discharge time values derived from this model, these values were also determined using electrochemical impedance spectroscopy. The results obtained from both methods are in close agreement, further validating the reliability of the model. Controlling substrate bias during sputtering allows us to reach a wide range of maximum stored charges as well as time associated with charge/discharge. Vanadium nitride thin films sputtered without substrate bias are suitable for microdevices requiring high energy, while those sputtered with higher substrate bias offer high power capabilities, making vanadium nitride a versatile material for energy storage in microdevices.

Conclusions

This study investigates the microstructural and electrochemical properties of sputtered vanadium nitride thin films prepared with various substrate bias voltages. Various techniques including SEM, AFM, XRD, XPS, CV, and four-point probe conductivity measurements were used to investigate the effects of substrate bias voltage on VN microstructure and composition. Here, we evidenced amorphization and densification processes of the VN films due to atomic peening effect at high substrate bias voltage. This was confirmed by electrochemical measurements in organic media, which revealed a decrease of the capacitive charge storage, e.g. decreased specific surface area, with increasing bias voltages.

Vanadium nitride electrochemical performance in 1 M KOH as a function of substrate bias voltage used during thin film deposition, combined with a semi-empirical fitting model, revealed that films sputtered with low substrate bias voltages (0 V and −50 V) exhibit higher capacity at low scan rates but have higher characteristic times associated with charge/discharge, whereas those sputtered with high bias voltages (−100 V to −200 V) exhibit lower capacity and lower characteristic times associated with charge/discharge. Indeed, the capacity and characteristic times associated with charge/discharge of those films are closely linked to the microstructure, especially the porosity/density and crystallinity, which have direct impact on the electrode conductivity. Porous and crystalline thin films provide high capacity due to high specific surface, while dense and amorphous films provide low characteristic times associated with charge/discharge due to higher electronic conductivity. Hence, a trade-off to optimize the capacity and characteristic time associated with charge/discharge can be obtained by modifying the substrate bias voltage. Notably, films sputtered with −50 V bias voltage demonstrated optimal electrochemical performance, with a capacity of 12 $mC.cm^{-2}$ (equivalent to 510 $C.cm^{-3}$ or 520 $F.cm^{-3}$) and a characteristic time associated with charge/discharge of 1.25 s, suggesting suitability for practical use as micro-supercapacitor electrodes with fast charge capability.

Acknowledgments

Labex STORE-EX (ANR-10-LABX-76–01) and Conseil Régional des Pays de la Loire are acknowledged for financial support (PhD grant AL). The research conducted in this publication was jointly funded by the Irish Research Council (IRC), the French Ministries of Europe and Foreign Affairs (MEAE) and Higher Education and Research (MESR) under grant PHC (Partenariat Hubert Curien) Ulysses 2022 entitled "Quantifying the factors limiting rate performance in supercapacitor electrodes").

ORCID

Thierry Brousse https://orcid.org/0000-0002-1715-0377

References

1. Y. Fu, Y. Peng, L. Zhao, and F. Ran, "Recent advances of fabricating vanadium nitride nanocompositions for high-performance anode materials of supercapacitors." *Journal of Energy Storage.*, **75**, 109564 (2024).
2. H.-H. Liu, H.-L. Zhang, H.-B. Xu, T.-P. Lou, Z.-T. Sui, and Y. Zhang, "Influence of the concentration of electrolyte on the capacitive properties of vanadium nitride electrode for electrochemical capacitors." *J. Electrochem. Soc.*, **165**, A97 (2018).
3. E. Le Calvez et al., "Influence of ion implantation on the charge storage mechanism of vanadium nitride pseudocapacitive thin films." *Electrochem. Commun.*, **125**, 107016 (2021).
4. A. Jrondi et al., "Major improvement in the cycling ability of pseudocapacitive vanadium nitride films for micro-supercapacitor." *Adv. Energy Mater.*, **13**, 2203462 (2023).
5. N. Ouldhamadouche et al., "Electrodes based on nano-tree-like vanadium nitride and carbon nanotubes for micro-supercapacitors." *Journal of Materials Science & Technology*, **34**, 976 (2018).
6. A. Achour, R. Lucio-Porto, S. Solaymani, M. Islam, I. Ahmad, and T. Brousse, "Reactive sputtering of vanadium nitride thin films as pseudo-capacitor electrodes for high areal capacitance and cyclic stability." *J. Mater. Sci: Mater. Electron.*, **29**, 13125 (2018).
7. O. Bondarchuk, A. Morel, D. Bélanger, E. Goikolea, T. Brousse, and R. Mysyk, "Thin films of pure vanadium nitride: evidence for anomalous non-faradaic capacitance." *J. Power Sources*, **324**, 439 (2016).
8. K. Robert et al., "On chip interdigitated micro-supercapacitors based on sputtered bifunctional vanadium nitride thin films with finely tuned inter- and intracolumnar porosities." *Adv Mater Technol. juill*, **3**, 1800036 (2018).
9. N. Witit-Anun and A. Buranawong, "Effect of sputtering power on the structure of DC magnetron sputtered vanadium nitride thin films." *J. Met. Mater. Miner.*, **27**, 47 (2017).
10. J. C. Caicedo, G. Zambrano, W. Aperador, L. Escobar-Alarcon, and E. Camps, "Mechanical and electrochemical characterization of vanadium nitride (VN) thin films." *Appl. Surf. Sci.*, **258**, 312 (2011).
11. C. Choi, K. Robert, G. Whang, P. Roussel, C. Lethien, and B. Dunn, "Photopatternable hydroxide ion electrolyte for solid-state micro-supercapacitors." *Joule*, **5**, 2466 (2021).
12. K. Robert et al., "Novel insights into the charge storage mechanism in pseudocapacitive vanadium nitride thick films for high-performance on-chip micro-supercapacitors." *Energy Environ. Sci.*, **13**, 949 (2020).
13. D. V. Horváth, J. Coelho, R. Tian, V. Nicolosi, and J. N. Coleman, "Quantifying the dependence of battery rate performance on electrode thickness." *ACS Appl. Energy Mater.*, **3**, 10154 (2020).
14. R. Tian et al., "Quantifying the effect of electronic conductivity on the rate performance of nanocomposite battery electrodes." *ACS Appl. Energy Mater.*, **3**, 2966 (2020).
15. R. Tian et al., "Quantifying the factors limiting rate performance in battery electrodes." *Nat. Commun.*, **10**, 1933 (2019).
16. Z. Ling et al., "Quantifying the role of nanotubes in nano:nano composite supercapacitor electrodes." *Adv. Energy Mater.*, **8**, 1702364 (2018).
17. A. Lebreton et al., "Control of microstructure and composition of reactively sputtered vanadium nitride thin films based on hysteresis curves and application to microsupercapacitors." *Journal of Vacuum Science & Technology A*, **42**, 023405 (2024).
18. N. Fairley et al., "Systematic and collaborative approach to problem solving using X-ray photoelectron spectroscopy." *Applied Surface Science Advances*, **5**, 100112 (2021).
19. A. Morel, Y. Borjon-Piron, R. L. Porto, T. Brousse, and D. Bélanger, "Suitable conditions for the use of vanadium nitride as an electrode for electrochemical capacitor." *J. Electrochem. Soc.*, **163**, A1077 (2016).
20. A. C. García-Wong et al., "Surface morphology-optical properties relationship in thermochromic VO2 thin films obtained by air oxidation of vanadium nitride." *Journal of Materiomics*, **7**, 657 (2021).
21. J. H. Huang, "Texture evolution of vanadium nitride thin films." *Thin Solid Films*, **688**, 137415 (2019).
22. D. Lundin, T. Minea, and J. T. Gudmundsson, *High Power Impulse Magnetron Sputtering: Fundamentals, Technologies, Challenges and Applications* (Elsevier, Amsterdam) p. 384 (2020).
23. H. Hajihoseini, M. Kateb, S. Ingvarsson, and J. T. Gudmundsson, "Effect of substrate bias on properties of HiPIMS deposited vanadium nitride films." *Thin Solid Films*, **663**, 126 (2018).
24. J. Keraudy, D. T. Nguyen, A. Ferrec, and P. Y. Jouan, "Comparison between DC and HiPIMS discharges. application to nickel thin films." *Advances in Engineering Research and Application*, ed. H. Fujita et al. (Springer International Publishing) 63, 196 (2019), [Internet][cité 11 déc 2024] (Lecture Notes in Networks and Systems Disponible sur http://link.springer.com.

25. R. Adalati et al., "Metal nitrides as efficient electrode material for supercapacitors: a review." *Journal of Energy Storage*, **56**, 105912 (2022).
26. M. C. Biesinger, "Advanced studies of transition metal X-ray photoelectron spectra." *PhD thesis*, University of South Australia (2012).
27. M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, and Smart, "RStC. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni." *Appl. Surf. Sci.*, **257**, 2717 (2011).
28. Y. Zhu et al., "Electron delocalization and electrochemical potential distribution phenomena in faradaic electrode materials for understanding electrochemical behavior." *Adv. Energy Mater.*, 2304317 (2024).
29. C. G. Zoski, "Transferred to digital print." *Handbook of Electrochemistry* (Elsevier, Amsterdam Heidelberg) p. 892 (2007).
30. A. Lebreton, J. Barbé, C. Lethien, J. N. Coleman, and T. Brousse, "Tuning deposition conditions for VN thin films electrodes for microsupercapacitors: influence of the thickness." *J. Electrochem. Soc.*, **2**, 171 090513 (2024).
31. H. Dinh Khac et al., "Nanofeather ruthenium nitride electrodes for electrochemical capacitors." *Nat. Mater.*, **23**, 670 (2024).
32. E. Haye et al., "Enhancing cycling stability and specific capacitance of vanadium nitride electrodes by tuning electrolyte composition." *J. Electrochem. Soc.*, **1**, 169 063503 (2022).