Enhancing Cycling Stability and Specific Capacitance of Vanadium Nitride Electrodes by Tuning Electrolyte Composition

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Enhancing Cycling Stability and Specific Capacitance of Vanadium Nitride Electrodes by Tuning Electrolyte Composition

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Abstract

In this study, the tuning of the KOH electrolyte composition is proposed as a strategy to drastically limit the capacitance fade of vanadium nitride (VN) electrode. We demonstrate that the use of a V^{5+} (as VO_4^{3-} vanadates anions) containing KOH electrolyte enhances the cycling stability of VN thin film electrode : a loss of 59% of

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the capacitance is observed for the electrode tested in KOH over 3000 consecutive cycles. After V^{5+} addition in the electrolyte, the capacitance fade is decreased to 23%. Furthermore, the presence of V^{5+} species in the solution leads to VN capacitance enhancement from 379 mF cm^{-2} for V^{5+} ions free electrolyte up to 577 mF cm^{-2} at 5 mV s^{-1} for V^{5+}-containing KOH solution. The enhanced cycling stability is attributed to the stabilization of an oxide/oxynitride layer at the VN surface, instead of its dissolution, thanks to the chemical equilibrium shift of the VN dissolution reaction. This simple and innovative strategy consisting in tuning the electrolyte composition opens new pathways for other systems that suffer from electrode dissolution in the electrolyte while being electrochemically cycled.

Introduction

Recently, vanadium nitride (VN) has been identified as one of the most promising transition metal compound for use in electrochemical capacitors (ECs) with a specific capacitance as high as 1340 F g^{-1} in a KOH electrolyte solution [1–12]. This impressive capacitance has been attributed to a combination of both a double layer-type capacitance and a pseudo-capacitance occurring at this nitride surface [2,6,13]. However, VN suffers from poor cycling stability, which hinders its practical use [14]. In the related literature, this poor cycling ability has been ascribed to the dissolution and non-stability of the vanadium oxide layer at the surface region, which is responsible for the pseudo-capacitive behaviour [2,5]. In order to cure such cycling instability limitation, Morel *et al*. [8] have proposed to decrease the applied potential window (V) from [-1.2:0V] to [-1.0:-0.4V] for VN electrode in KOH electrolyte. Although a cycling stability over 10.000 cycles has been achieved, this led, however, to an energy density reduction by a factor of 4 for symmetrical VN devices, due to this narrow potential window. Recently, the stability enhancement of VN in K_2SO_4 electrolyte has been

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reported [4]. However, the specific capacitance in this neutral electrolyte is almost five times lower compared to that of the same VN electrode tested in KOH electrolyte [5,6]. Despite the fact that VN is electrochemically unstable in aqueous alkaline electrolytes including KOH, this type of electrolyte offers the best capacitance performance due to fast reversible redox reactions, involving surface oxide groups and OH^- ions from the electrolyte [2,15]. To the best of our knowledge, only Lu *et al.* [16] have stabilized VN electrode over a relatively large number of charge/discharge cycles (15000 cycles with 88% retention) in KOH electrolyte by coating VN with an ultra-thin carbon layer, without sacrificing the capacitance or energy density. In the present study, a new strategy is proposed to limit the capacitance loss of VN that can complement the previously reported methods. Indeed, the decline of VN capacitance involves the loss of V^{5+} and/or V^{4+} ions by dissolution from the oxide layer at the oxidized surface region of the VN compound [2,4,5]. We demonstrate that the use of a V^{5+}-containing KOH electrolyte offers a simple, yet effective, strategy to suppress the capacitance loss of VN. We also report on the effect of the V^{5+} species in the electrolyte on the enhancement of the specific capacitance of the VN electrodes by more than 1.5-fold compared to the electrolyte without V^{5+} species.

Materials and methods

VN films were deposited on silicon substrates by reactive magnetron sputtering of a rectangular vanadium target (330x50x6 mm) in a gas mixture of Ar/N_2 using a semi-industrial sputtering machine (Vinci Technologies). The target-substrate distance was 5 cm, with a back and forth movement of the substrate in front of the target. The current applied to the target was fixed to 1.5 A using a pulsed-DC Pinnacle/Advanced Energy power supply at 50 kHz, with t_{OFF} = 4 µs. The Ar and N_2 flow rates were kept at 30 and 5 sccm, respectively, leading to a total gas pressure of 1.1 Pa. No substrate bias was

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applied during deposition. After deposition, the morphology of the film was investigated by scanning electron microscopy (SEM), using a JEOL JSM 7500F microscope. The structure of the deposited films was assessed by X-ray diffraction (XRD) measurements on a PANalytical X'Pert PRO diffractometer, using Cu Kα radiation (1.5406 Å). The measurement was performed in a θ/θ-ω configuration, with an offset ω angle of 2° avoiding the strong diffraction of the silicon substrate. The chemical composition of the VN thin film was investigated before and after electrochemical tests by X-ray photoelectron spectroscopy (XPS), performed on a Thermo Scientific K-Alpha spectrometer (Al Kα at 1486.68 eV, spot size of 250×250 µm). No surface cleaning was performed before the analysis. A flood gun was applied for charge compensation. XPS depth profiling was used to reveal the chemical changes that occurred on the surface and the bulk of the material. An Ar^+ beam at 2 keV (raster size 1.25×1.25 mm², 30°, 3.3 µA) was used, with a step size of 20 s. The N 1s, O 1s and V 2p levels were recorded at a pass energy of 50 eV with a single scan. The authors are aware that ion beam may induce modification of chemical state, especially on vanadium. In this view, the conclusion is more oriented on element concentration rather than the changes of chemistry.

The electrochemical characterization was performed in a standard three-electrode cell system, in which VN (1×1 cm^2), Hg/HgO and platinum plates act respectively as working, reference and counter electrodes. The electrolyte was prepared by adding 0.05 or 0.1 M V_2O_5 into a 1 M KOH solution.

Cyclic voltammetry (CV) was conducted in a potential window from -0.9 to 0 V (*vs.* Hg/HgO) at different scan rates: 5, 10, 20, 50 and 100 mV s^{-1}.

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According to the Pourbaix diagram of vanadium (Figure 1), the dissolution of V_2O_5 powder in 1M KOH, namely at pH 14, leads to the formation of tetrahedral VO_4^{3-} vanadates ions, with V^{5+} oxidation state.

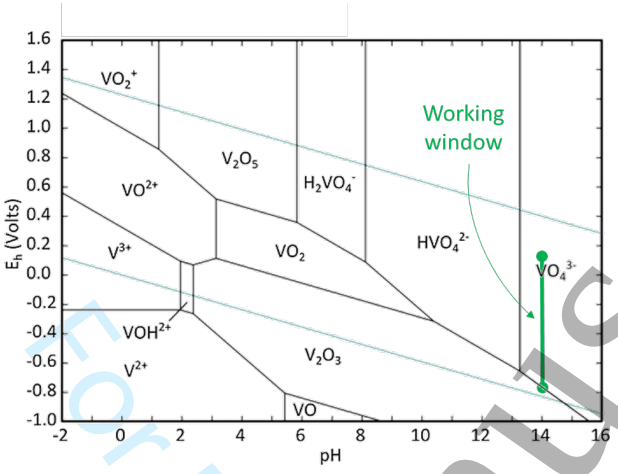

Figure 1. Pourbaix diagram of vanadium oxide with the working window, adapted from [17]

Galvanostatic charge discharge (GCD) measurements were carried out at current densities of 1, 2, 3, 5 and 10 mA cm^{-2}, in a potential window from -0.8 to 0 V.

Electrochemical Impedance spectroscopy (EIS) was performed in the frequency range of 100 kHz to 0.01 Hz with a 10 mV ac amplitude.

The average specific capacitance was calculated from the cyclic voltammetry (CV) plots, using the following equation:

$$C_{sq}(mF \cdot cm^{-2}) = \frac{\int I\, dV}{\Delta V \times v}$$

where *I* represents the oxidation current density, and ΔV is the potential window, v is the scanning rate. For some distorted CVs obtained at fast scan rates, the same equation was used although this is quite difficult to provide a capacitance value in such

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case, and this was done for comparison purpose only with the values determined at low scan rates.

The average specific capacitance was calculated from the galvanostatic discharge curves, using the following equation:

$$C_{sq}(mF \cdot cm^{-2}) = \frac{I\Delta t}{\Delta V \times A}$$

Where *I* denotes the current density, Δt is the discharge time, and ΔV is the width of the potential window during discharge, *A* is the area of active materials.

Faradaic efficiency were calculated from the galvanostatic charge and discharge curves, using the following equation:

$$\text{Faradaic efficiency} = \frac{\text{t(discharge)}}{\text{t(charge)}} \times 100\%$$

Results and discussion

The morphology and structure of the VN electrodes are presented in **Figure 2**. From the top and cross section SEM observations (**Figure 2** a and b), a homogeneous columnar microstructure is observed, with cubic crystallites pointing at the surface, in agreement with previous works on transition metal nitride thin films, deposited without substrate bias [18,19]. The good crystallinity of the film is confirmed by XRD measurement (**Figure 2**.c), with an intense peak at 37.6°, attributed to the (111) peak of cubic VN [20]. Such a strong (111) preferred orientation is typical for transition metal nitride films deposited without bias. The crystallite size is around 22 nm, as estimated from the Debye-Scherrer formula, in agreement with SEM observation. The film thickness determined from the cross-section SEM image is around 550 nm.

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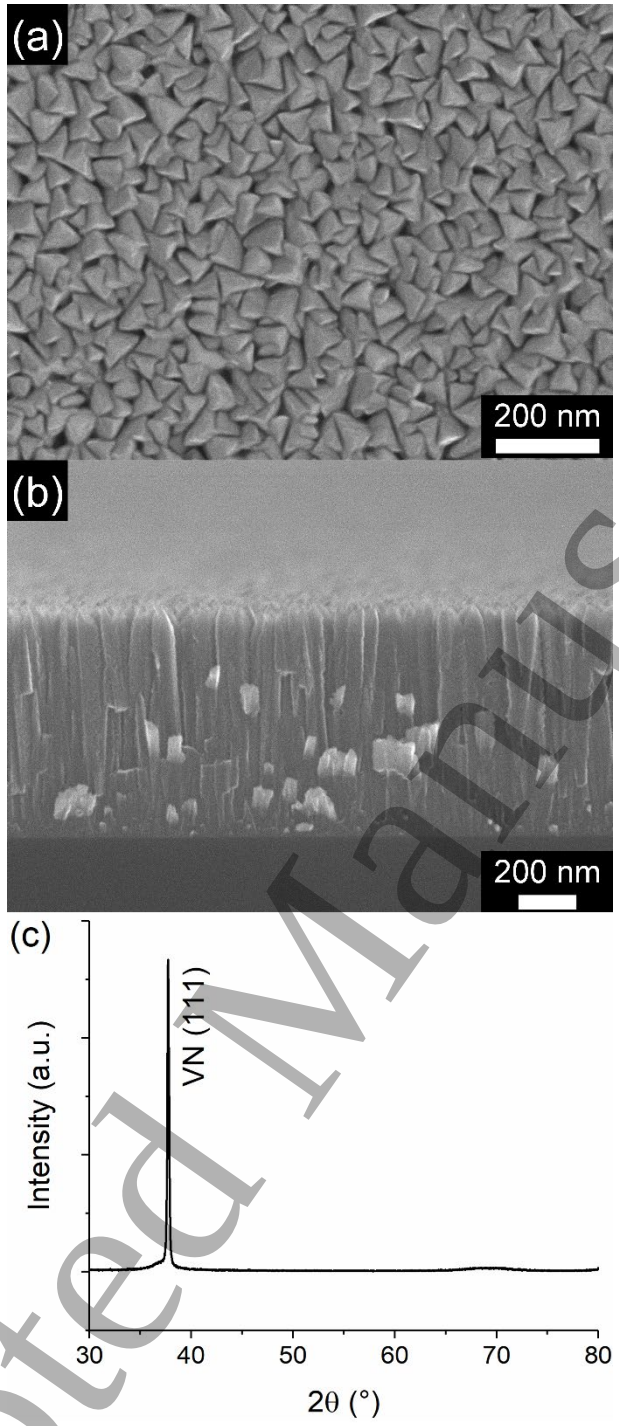

Figure 2. (a) top and (b) cross section SEM observations, and (c) XRD pattern of the VN electrode.

The electrochemical behavior of the VN electrodes were assessed in 1 M KOH aqueous solution with or without the addition of V_2O_5 in a usual 3-electrode cell. The cyclic voltammograms (CV) of the VN film in 1 M KOH, 1 M KOH + 0.05 M V_2O_5 and 1 M KOH + 0.1 M V_2O_5 as a function of scan rate in the potential range of -0.9 to 0 V

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are presented in **Figure 3**. The VN films show a pseudocapacitive behaviour under all tested conditions. Obviously, the specific capacitance of the VN electrode in 1 M KOH aqueous solution decreases from 379 to 154 mF cm^{-2} (Table 1, **Figure 4**) upon increasing the scan rate from 5 to 100 mV s^{-1}, while the shape of the CVs remains almost unaltered, suggesting that the electrode owns a good rate capability. Distortion is noted at high scan rate, indicating the loss of capacitive behaviour, but the specific capacitance is still given for comparative purpose.

A low potential (between -0.9 and -0.8 V vs Hg/HgO), a slight current density variation is observed, due to some reduction of VO_4^{3-} (with V^{5+}) into V_2O_3 (with V^{3+}), in accordance with the Pourbaix diagram (Figure 1).

Addition of V_2O_5 in the electrolyte promotes a significant increase of the specific capacitance (*Cs*) for all investigated scan rates under our experimental conditions, although a slight distortion of the CVs was observed. Indeed, addition of V_2O_5 in the electrolytic solution (1 M KOH) led to an increase of the specific capacitance from 379 mF cm^{-2} (1 M KOH) to 471 mF cm^{-2} (1 M KOH + 0.05 M V_2O_5) and 577 mF cm^{-2} (1 M KOH + 0.1 M V_2O_5) at a sweep rate of 5 mV s^{-1}. This behaviour is most likely due to reduced effective interaction between the electrode surface and OH^- anions at higher scan rates.

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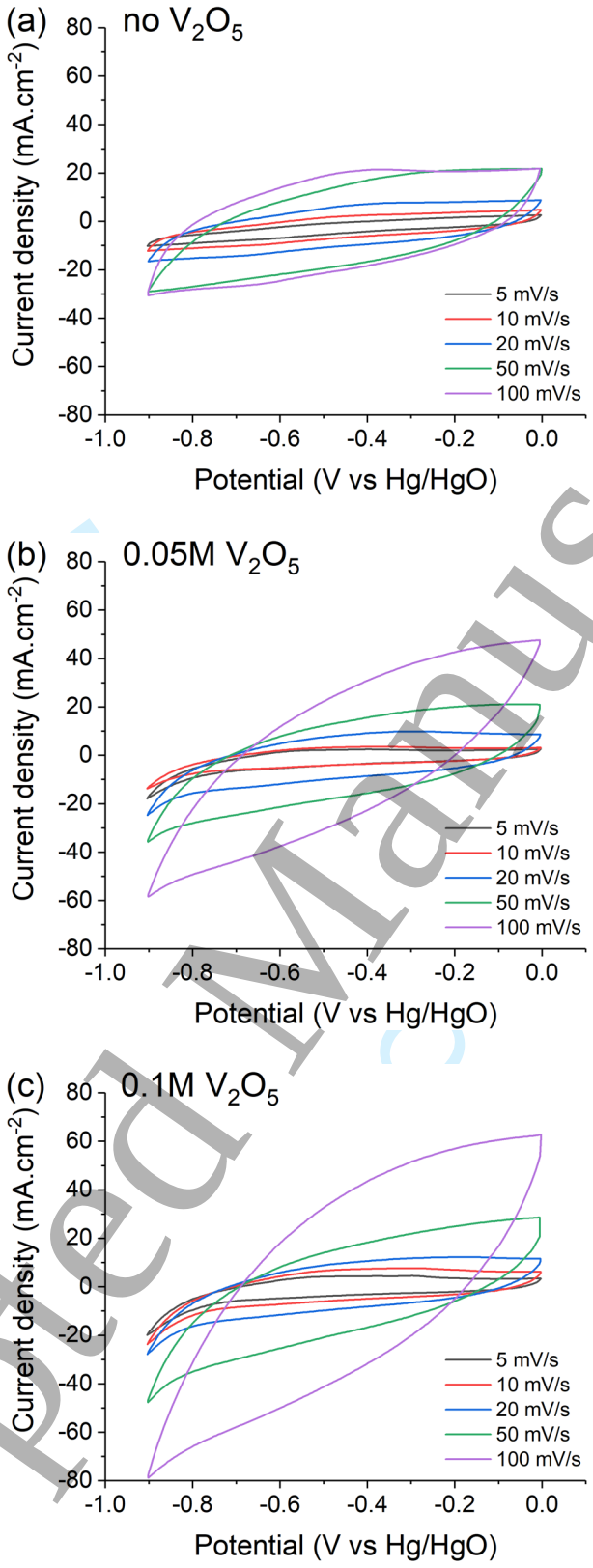

Figure 3. Cyclic voltammetric curves of VN electrodes in (a) 1 M KOH, (b) 1 M KOH + 0.05M V_2O_5 and (c) 1 M KOH + 0.1 M V_2O_5 at scan rates of 5, 10, 20, 50 and 100 mV s^{-1}

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Table 1. The values of the specific capacitance Cs *versus* scan rate of the VN electrodes in KOH without and with, 0.05M, and 0.1 M V_2O_5

Scan rate (**mV s^{-1}**)	**C_s (mF cm^{-2})** in 1 M KOH	**C_s (mF cm^{-2})** in 1 M KOH + 0.05M V_2O_5	**C_s (mF cm^{-2})** in 1 M KOH + 0.1 M V_2O_5
5	379	471	577
10	364	402	464
20	329	338	361
50	254	245	278
100	154	196	276

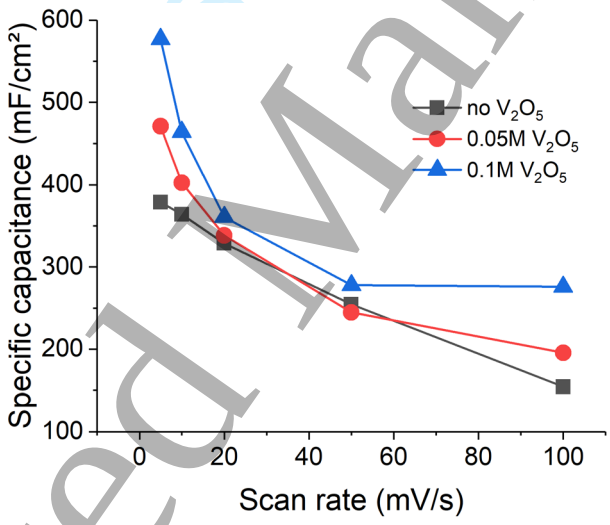

Figure 4. Evolution of the specific capacitance of VN at different scan rates in different KOH electrolytes.

The corresponding galvanostatic charge-discharge plots at a current densities of 1, 2, 3, 5 and 10 mA/cm² in the -0.8 to 0 V range are shown in **Figure 5** while the calculated specific capacitance values are summarized in Table 2. No significant IR drop was reported, as in the case of CrN [21], indicating a better conductivity. A similar trend –

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i.e. a decrease of the specific capacitance values – was evidenced in all systems upon increasing the current density. Generally, the retention of the specific capacitance with current density depends on: i) diffusion of ions in electrolyte, ii) adsorption of ions on the electrode surface, and iii) charge transfer between electrode and electrolyte. Enhancing the current density could slow any of the above-mentioned conditions, leading to the decrease of the specific capacitance.

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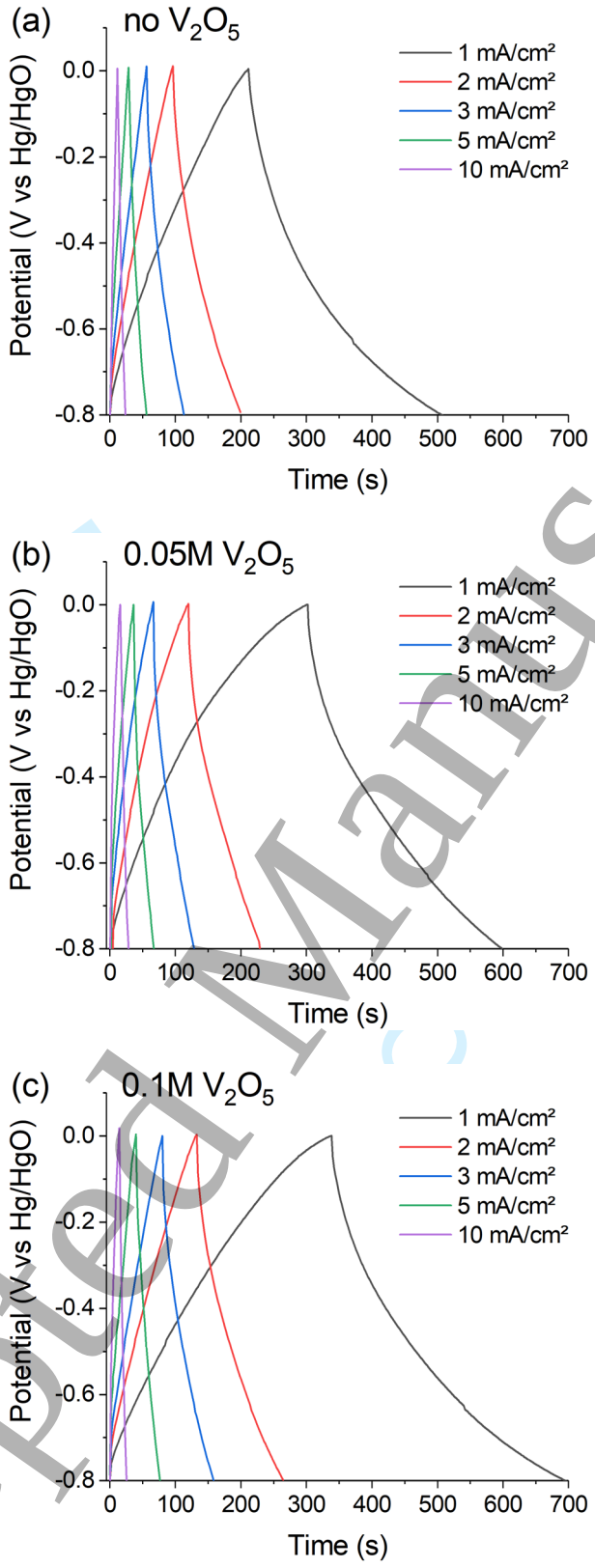

Figure 5. Galvanostatic charge discharge curves of VN electrodes in (a) 1 M KOH, (b) 1 M KOH + 0.05M V_2O_5 and (c) 1 M KOH + 0.1 M V_2O_5 at current densities of 1, 2, 3, 5 and 10 $mA.cm^{-2}$.

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Table 2. The values of Cs as a function of current density of the VN electrodes in 1 M KOH without and with 0.05M, and 0.1 M of V_2O_5.

Current density (mA/cm^2)	**Cs ($mF\ cm^{-2}$)** in 1 M KOH	**Cs ($mF\ cm^{-2}$)** In 1 M KOH + 0.05M V_2O_5	**Cs ($mF\ cm^{-2}$)** in 1 M KOH + 0.1 M V_2O_5
1	373	371	456
2	260	273	330
3	218	236	300
5	177	194	231
10	150	169	153

In order to gain a better understanding on the electrochemical behaviour of the electrode/electrolyte interface during the charge storage process, electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 100 kHz to 0.01 Hz in 1 M KOH (**Figure 6**). The equivalent Randles circuit of the Nyquist plot is shown in the inset of Figure 5 and includes a solution resistance (R_s), constant phase element (CPE), charge transfer resistance (R_{ct}) and Warburg element (W), with values presented in Table 3. The EIS analysis revealed that the Nyquist plots are similar in shape and exhibit a small semicircle at high frequency region and a slope line (Warburg curve) in the low frequency region.

The low resistance values in the 1 M KOH + 0.1 M V_2O_5 electrolyte correlate with enhanced conductivity of the VN electrode when V_2O_5 is dissolved in the electrolytic solution to provide VO_4^{3-} vanadates ions.

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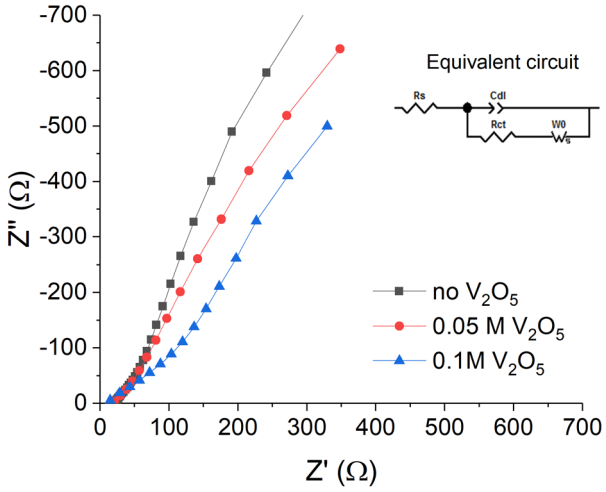

Figure 6. Electrochemical Impedance spectroscopy (EIS) measurements of the VN electrodes in different KOH electrolytes and their EIS equivalent circuit in 1 M KOH aqueous solution without and with 0.05M, and 0.1 M V_2O_5

Table 3. R_{ct} and R_s values of VN electrodes in 1 M KOH without and with 0.05M, and 0.1 M V_2O_5

EIS	R_s (Ω)	R_{ct} (Ω)
VN in bare 1KOH	17.12	260
VN in 1 M KOH with 0.05M V_2O_5	17.45	240.3
VN in 1 M KOH with 0.1 M V_2O_5	17.25	140.7

Finally, the cycling stability of the VN electrodes was investigated in the different electrolytic solutions, namely, 1 M KOH, 1 M KOH+0.05 M V_2O_5 and KOH+0.1 M V_2O_5 in the potential window of -0.9 to 0V at a scan rate of 50 mV s^{-1} (**Figure 6**). All the capacitance values experienced a continuous decrease for the first 1600 cycles then remained almost unaffected up to 3000 cycles. The most important feature of this figure is the highest retention (77%) of the initial capacitance recorded for the VN

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electrode in 1 M KOH + 0.1 M V_2O_5, as compared to retention of 60% and 41% achieved in the 1 M KOH + 0.05 V_2O_5 and 1 M KOH solutions, respectively (Table 4). Again, these results again evidence the improvement of the energy storage performance and stability of the VN electrode by simply altering the composition of the electrolytic solution through the addition of vanadates ions.

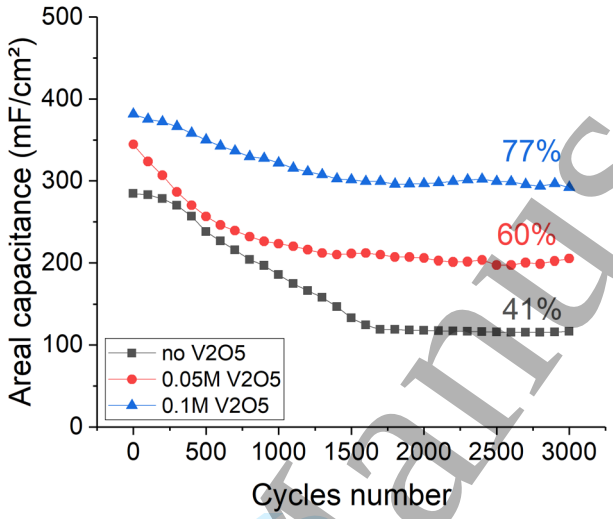

Figure 6. Evolution of the areal capacitance *vs.* the number of cycles of the VN electrode in the different KOH electrolytes for 3000 cycles (potential window: –0.9 to 0V (vs. Hg/HgO), scanning rate: 50 mV s^{-1}).

Table 4. Cycling stability of the VN electrodes in 1 M KOH without and with 0.05 M, and 0.1 M V_2O_5

Electrolyte	**Cs initial** (mF cm^{-2})	**Cs after 3000 cycles** (mF cm^{-2})	**Cs retention** (%)
1 M KOH	284	117	41
1 M KOH + 0.05M V_2O_5	345	205	60
1 M KOH + 0.1 M V_2O_5	381	292	77

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To investigate the origin of the modification of the charge storage by adding V_2O_5 in 1 M KOH electrolyte, XPS analyses were performed on the VN electrodes before and after cycling. The electrodes were etched using argon plasma to record depth profiles during 350s, corresponding to a depth of 100 nm. It is important to remember that the film presents a porous columnar microstructure, as shown on the SEM observation (**Figure 2**). **Figure 7** depicts the O 1s and V 2p core levels spectra within the coating (etching time 350s) and on the surface (etching time 20s) for VN film after deposition and after cycling in 1 M KOH, 1 M KOH+0.05 M V_2O_5 and KOH+0.1 M V_2O_5. The very first spectra are not presented as the signal heavily depends on surface contamination, especially after electrochemical tests. Although it is delicate to identify the chemical state of vanadium because of potential ion beam induced damages, it is clear that the bulk (Figure 7.a) and the surface (Figure 7.b) contain more oxygen (and thus more oxidized species) when the electrodes are cycled in KOH containing V_2O_5.

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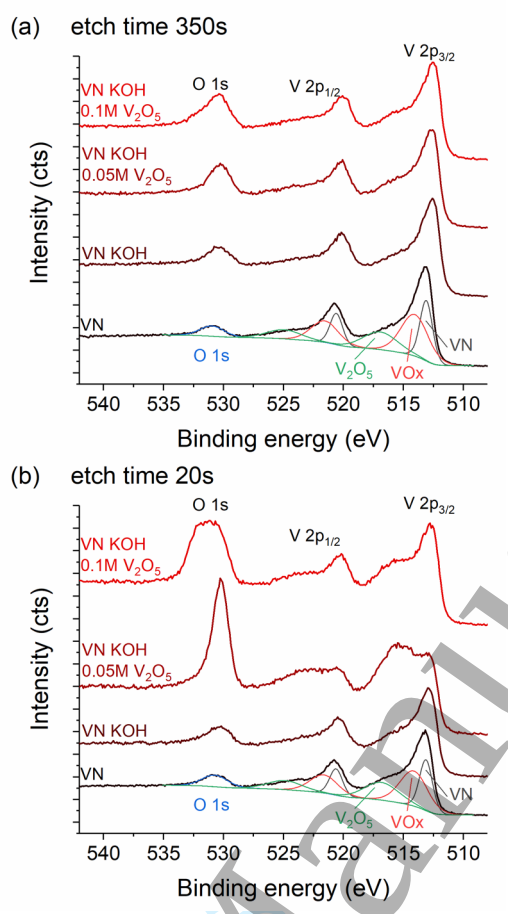

Figure 7. O 1s and V 2p core level spectra of VN electrodes before and after cycling in the different KOH electrolytes, (a) in the bulk (etching time 350s) and (b) at the surface (etching time 20s)

The entire XPS depth profiles (Figure S1) and the concentration evolutions of O 1s and V 2p contributions (Figure S2) are given in the supplementary information. One can note that the as-deposited VN electrode is nearly stoichiometric, with a nitrogen concentration of ≈40% vanadium content of ≈50%, and an oxygen content of ≈10%. Such oxygen content is often observed in TMN nitride deposited by PVD [18]. The oxygen content within the coating (signal averaged from 100 to 300s of the profile) increases to about 16, 25 and 28 at.% after cycling in 1 M KOH, 1 M KOH + 0.05 M V_2O_5 and 1 M KOH + 0.1 M V_2O_5, respectively. At the same time, the nitrogen content decreases from 40 to 28% for 1 M KOH + 0.1 M V_2O_5 electrolyte. Concerning the signal

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of vanadium, the two oxide peaks at 514.0±0.1 and 517.0±0.1 eV, respectively attributed to VO_x (with $x\approx2$) and V_2O_5 are more intense at the surface, when cycled in the V_2O_5-containing electrolyte.

The understanding of surface mechanisms when the VN electrode is cycled in V_2O_5-containing electrolyte is not obvious. First, the dissolution of V_2O_5 leads to the presence of vanadates VO_4^{3-} ions, with V^{5+} oxidation state, according to Pourbaix diagram (Figure 1). However, during the cycling, an equilibrium between V^{3+} from the electrode surface and V^{5+} from the electrolyte is established on the electrode surface, which is out of the thermodynamic equilibrium. These redox reactions are randomly occurring at the surface of the electrode which explains the distribution of potential observed from the CVs, which is typically observed for pseudocapacitive electrodes[22,23] . It does not seem that preferential sites are involved since the redox reactions do not translate in a well-defined pair of redox peaks on the CVs.

In the working conditions, VN (where V oxidation state is +3) tends to dissolve into the KOH electrolyte to form VO_4^{3-} ions (with V^{5+} oxidation state), as it is the most stable specie according to the Pourbaix diagram. This dissolution probably occurs in two subsequent steps, with first surface oxidation of VN, followed by the oxide dissolution. This assumption is supported by the slight increase of oxygen content when comparing XPS depth profiles of as deposited VN and VN cycled in 1M KOH without V_2O_5 (Figure S1.a and b). Each of these steps are characterized by a rate constant and an equilibrium. The presence of vanadates ions in the electrolyte shift the equilibrium of surface oxide dissolution according to Le Chatelier principle. Then, the previous step, namely reversible surface oxidation, becomes predominant, and the oxide dissolution no longer occurs, resulting in the formation of thick surface oxide, as observed in XPS.

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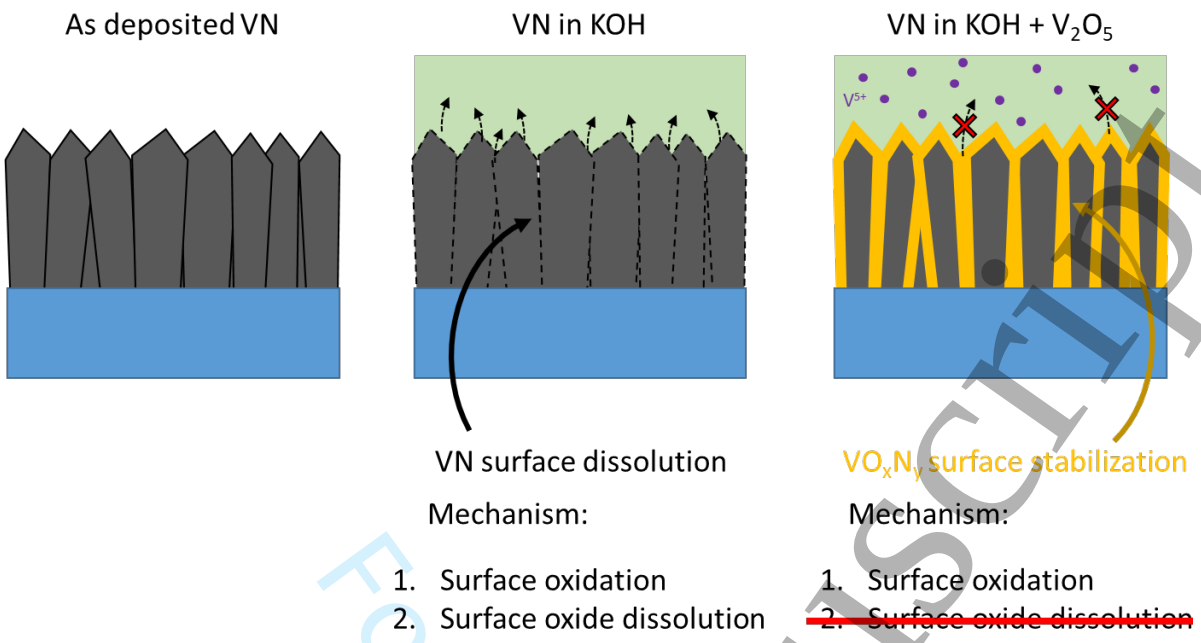

Figure 8. Sketch of surface evolution of VN film in different electrolytes. The thick yellow line corresponds to the stabilization of the oxide/oxynitride layer.

The **Figure 8** summarizes the surface evolution of VN, depending the electrolyte, with the stabilization of oxide/oxynitride layer. As the coating is highly porous, with columnar morphology, the formation of oxide occurs all along the column surface, resulting in the observation of high oxygen content even at high erosion time during XPS analysis. The distortion of the CV curves (**Figure 3**) in the presence of V_2O_5 also corroborates the higher resistivity of the oxide layer compared to VN.

Conclusion

In the present work, a new strategy is proposed to improve the cycling stability of vanadium nitride thin film in KOH, by adding V^{5+} ions in the electrolyte, introduced as VO_4^{3-} vanadate anions. According to Le Chatelier principles, the chemical equilibrium of the VN dissolution reaction is shifted, leading to the stabilization of an oxide/oxynitride layer at the VN surface. While the capacitance drops by 59% for VN

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in 1 M KOH, the drop can be limited to 23% in 1 M KOH + 0.1 M V_2O_5. Furthermore, a capacitance increase by the VN electrodes by more than 1.5 fold was observed upon V^{5+} saturation, although, a slight distortion of the CV curve was also noticed, may be due to the presence of more resistive oxide on VN surface. This simple and innovative strategy can be implemented for other systems that suffer from dissolution in the electrolytic solution.

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