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Sputtered vanadium carbon nitride (VCN) thin films: a potential electrode for supercapacitors

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E-mail: vijayprasath86@gmail.com**Keywords:** thin films, sputtering, supercapacitor, vanadium carbon nitride

Abstract

The preparation of efficient thin film-based electrode materials is a vital prerequisite for practical energy storage devices. Herein, we have prepared unique vanadium carbon nitride (VCN) thin films on FTO substrates by pulsed DC magnetron sputtering technique for competent supercapacitor electrodes. XRD analysis confirmed the crystalline nature of VCN thin films. SEM and AFM revealed a smooth morphology with an average grain size of 30 nm. Raman spectra showed two broad peaks around 1346 and 1589 cm^{-1} , belonging to the D-band and G-band of VCN. The surface electronic states of VCN were investigated by XPS analysis, which confirmed the formation of pure VCN films without any impurities. The electrochemical performance of the thin film electrode was evaluated using cyclic voltammetry (CV), Galvanostatic charge–discharge (GCD), and Electrochemical impedance analysis (EIS). The electrochemical results showed the VCN thin films exhibited super capacitive behaviours. The maximum specific capacitance (C_s) value of 78.2 F g^{-1} was obtained from GCD studies. A variation in charge transfer resistance is detected from the EIS study, which arises due to the partial oxidation of the active nitride component. The VCN electrode showed good cycling stability, retaining 87% of its capacitance at a current density of 5 A g^{-1} even after 2000 cycles. The sputtered VCN films have been demonstrated as potential thin film electrodes for electrochemical supercapacitors for practical energy storage devices.

1. Introduction

Increasing demands for portable electronics and the excessive consumption of non-renewable energy have prompted scientists to explore new energy storage devices that offer high power as well as energy density [1–4]. A supercapacitor (SC) has gained prominence in the area of energy storage as a result of its benefits, including fast rechargeability, extended cycle life, environmentally friendly nature, and high energy densities [5–7]. Although SCs are highly efficient, their low energy density severely impedes their commercialization. It is therefore imperative that effective strategies be developed to enhance the energy density of SCs while ensuring their power density. The preparation of cost-effective and highly efficient electrochemical capacitors (EC) with electrode materials having high electrical conductivity and excellent reversibility is of great importance.

In recent years, metal nitrides, which work as electrode material in supercapacitors, have been studied intensively owing to their extraordinary electrochemical properties, such as high specific capacities, high chemical stability, good thermal stability, and high electrical conductivity [8]. They have a high conductivity of 4000 to 55,000 s cm^{-1} and a tremendous power density. Commonly used metal nitrides are TiN, Mo_2N , VN, RuN, FeN, Ni_3N , TaN, NbN, etc [9–14]. Among these materials, vanadium nitride (VN) has emerged as a

dominant electrode material for SC since it has a larger specific capacitance (nearly 1340 Fg^{-1}) over carbon-based materials, and a higher electrical conductivity ($1.67 \times 10^6 \text{ Sm}^{-1}$) over transition metal sulphides [6], oxides [12, 14], and hydroxides [15]. Besides, the integrated VN/CF/Ni(OH) ASC module showed an improved energy density and cyclic stability [16]. Moreover, Ran *et al* developed an intercalation structure using VN NPs inserted into the GO layer. The resulting VN/GO had a high cycling stability with 93% capacitance retention over 5000 cycles and a high specific capacitance of 109.7 F g^{-1} [17]. Gao *et al* developed a unique method for fabricating a hybrid electrode consisting of VN nanodots intercalated in carbon nanosheets that had a high volumetric capacitance and good cycle stability [18]. Anusha Thampi *et al* sputtered TiVN based micro supercapacitors exhibiting a reasonable electrochemical capacity performance for microelectronics [19]. As a result, mixing carbon-based materials with VN NPs helps to increase the electrode material's specific capacitance and cycling stability [20–25]. The most widely used techniques for developing metal nitrides at the moment include (a) heating the metals or metals containing carbon to high temperatures in NH_3 or N_2 atmospheres; (b) high-pressure and high-temperature synthesis; (c) ammonolysis of oxides and binary compounds; (d) sol–gel method, (e) vapor deposition of metal-carbon nitride, (f) Solvothermal method, etc, [26, 27]. The conventional methods used to fabricate electrodes for electrochemical devices have several drawbacks, including insufficient bonding to an electrode, which raises peripheral resistance, and volume loss to the electrolyte [28, 29]. Techniques like sputtering, which is a physical vapor deposition (PVD) process, could be yet another way to deal with this problem. PVD develops thin films with high adhesion, perfect chemical stoichiometry, tuneable thickness, and structure.

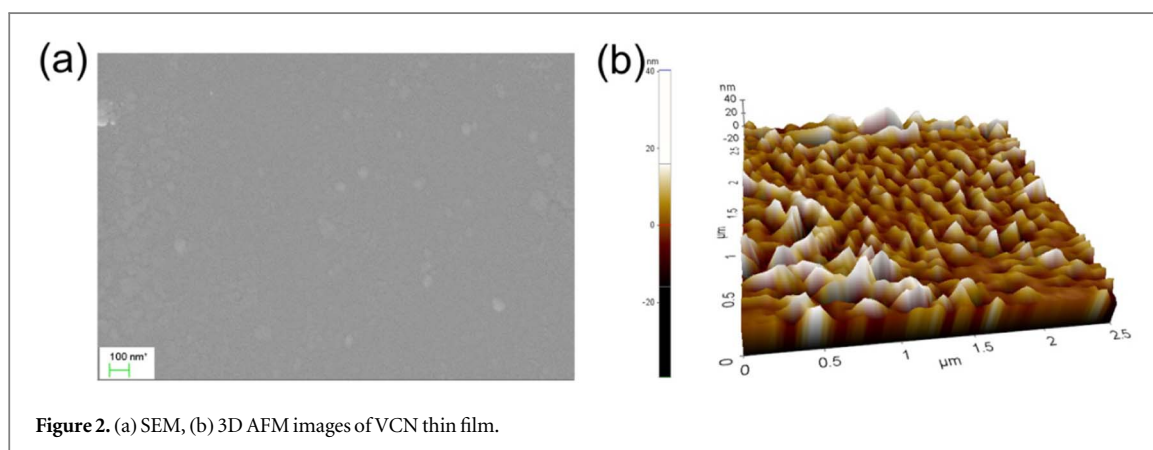
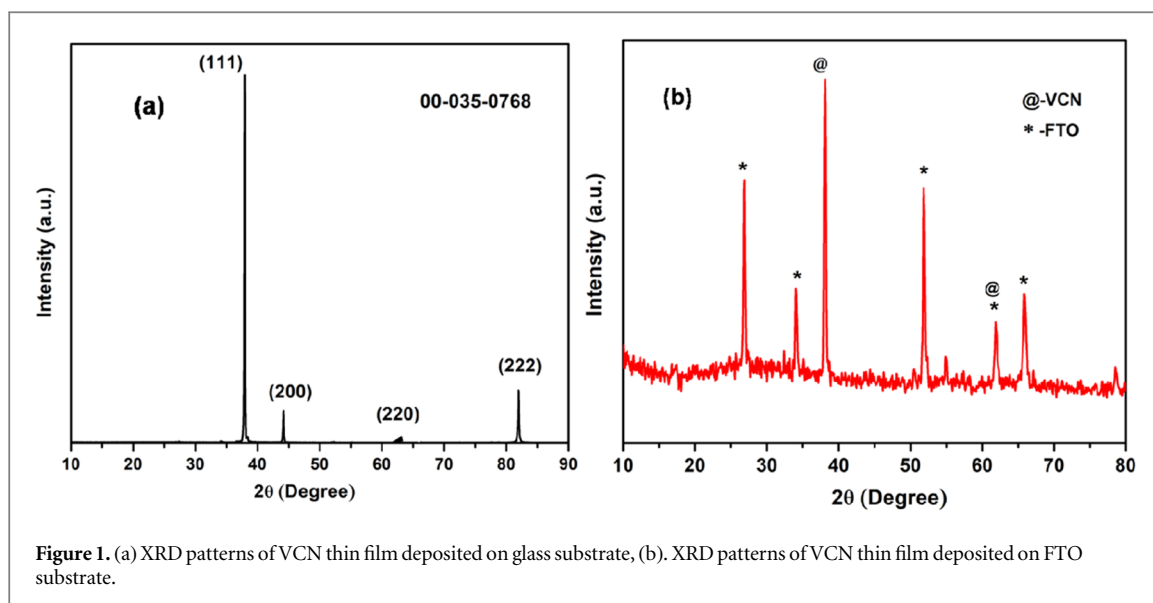
In light of the above reports, in the current work, thin films of vanadium carbon nitride composite have been fabricated on glass and FTO substrates via the Direct current (DC) sputtering method for supercapacitor applications.

2. Experimental

Thin films of vanadium carbon nitride were sputtered on glass and FTO substrates using the direct current (DC) reactive magnetron sputtering method. The deposition procedure was carried out in a sputtering chamber that has two target holders and a motorized substrate heater that oscillates between both target holders. Targets of Vanadium (V) (99.99% pure) and graphene (99.99% pure) were kept inside the sputtering chamber. Prior to the deposition, a vacuum state of 8×10^{-6} mbar was sustained inside the chamber. After that, highly pure inert argon gas & reactive nitrogen gas were inlet into the chamber until the deposition pressure (Ar + N) reached 5×10^{-3} mbar. Mass flow controllers coupled to the sputtering system kept the flow rate of N:Ar at 1:1. The deposition temperature was set at 400°C , and the sputtering powers have been tuned at 150 and 75 W for V and graphene targets, respectively. The obtained films were characterized by an x-ray diffractometer (model; X'PERT PRO PANalytical). The diffraction patterns were recorded in the range of 10° – 80° for the Iron oxide samples, where the monochromatic wavelength of $1.5406 \text{ \AA}$ was used. The morphology was examined with SEM (model: JEOL/EO-JSM-6390), vibrational through Raman (Horiba Jobin Yvon LabRAM HR), and XPS measurements were performed with an XPS instrument (Carl Zeiss) equipped with an Ultra 55 FESEM with EDS, and all the spectra were recorded under ultrahigh vacuum with $\text{Al K}\alpha$ excitation at 250 W.

3. Results and discussion

Figures 1(a) and (b) depict the XRD patterns of VCN grown on the glass and FTO substrates. The XRD spectra indicate that VCN thin films have been successfully grown by DC sputtering. For the film deposited on a glass substrate, aside from VCN (111), the peaks that were ascribed to other planes like (200), (220), and (222) were observed, and they match well with JCPDS-00–035–0768. For the film deposited on the FTO substrate, along with the (111) plane, (220) was also observed. Peaks corresponding to the substrates were also observed in the XRD-FTO patterns. The peak position of VCN (111) slightly varies across the sample. The variation in peak position may be due to the different strain levels in the sample. The strain was attributed to the lattice mismatch between the VCN thin films and substrates. Further, sharp diffraction peaks reveal the highly crystalline nature of the deposited films. These results showed that VCN thin films deposited on glass substrates have a relatively higher crystalline quality compared with VCN deposited over FTO substrates. Considering the peak intensity in the glass XRD spectra, the intensity of the VCN (111) peak is higher than that in the FTO substrate sample. Thus, the crystalline quality of the VCN thin film in the glass sample is higher than that of the FTO sample. The intensities of the XRD peaks were compared, assuming that the thicknesses of the VCN thin films of both samples were the same because they were deposited at the same time through the same DC sputtering system. Therefore, only thin films with a higher crystalline quality allow a higher x-ray intensity to be reflected back to the detector [30].



The morphology of VCN thin films was examined using SEM and AFM analysis. SEM image of VCN (figure 2(a)) shows smooth morphology with small grains over the surface. Figure 2(b) depicts the 3D AFM image of VCN film. The surface of the prepared film exhibited a smooth morphology with a roughness value of less than 4 nm. It is clear that the grain growth is compact and homogeneous, with an average grain size of 30 nm.

Raman spectroscopy is a non-destructive fingerprint tool to examine the chemical structure of samples. Figure 3 shows the Raman bands stimulated by the molecular vibrations of VCN thin films deposited over glass and FTO substrates. The observed bands were fitted using the Lorentzian function. Two broad peaks were observed for samples deposited on both substrates around 1346 and 1589 cm^{-1} , which belong to the D band and G-band [31] of VCN. Samples deposited on glass substrates showed more intense Raman peaks than samples deposited on FTO substrates. This infers that the sample deposited on glass possesses long-range translational symmetry and is highly crystalline nature. These observations are consistent with our XRD results. Hang Cheng *et al* observed peaks around 1310 and 1505 cm^{-1} for vanadium nitrate-hard carbon composites (VN-HC composites) [31]. Hence, Raman spectra suggest the presence of vanadium carbon nitride composite.

The surface electronic states of the VCN composite were investigated by x-ray photoelectron spectroscopy (XPS) (figure 4). As given in figure 4(a), the C1s shows a peak at 284.6 eV which is attributed to the sp^2 carbon, C–C, while the peak observed at a higher binding energy of 285.4 eV belongs to the sp^3 carbon, C–N [32]. The N 1s spectrum (figure 4(b)) shows a broad peak at 398.5 eV, which belongs to metal N, and the detected peak around 400 eV belongs to quaternary N [33]. In V 2p spectra, three peaks were identified. The peak detected at 513.1 eV is imputed to V–N, signifying the formation of VN, whereas the peaks identified at 514.6 and 518.8 eV correspond to V–N–O and V–O, respectively [34]. Additionally, the peaks detected near 525 eV and 530 eV in the O1s spectra correspond to V–O and V–O–N [35]. The XPS analysis again confirms the formation of VCN thin films.

The electrochemical properties of the VCN thin film coated on an FTO substrate were studied by the Bio-logic SP-150 electrochemical workstation. The sputtered VCN film coated on FTO was the working electrode,

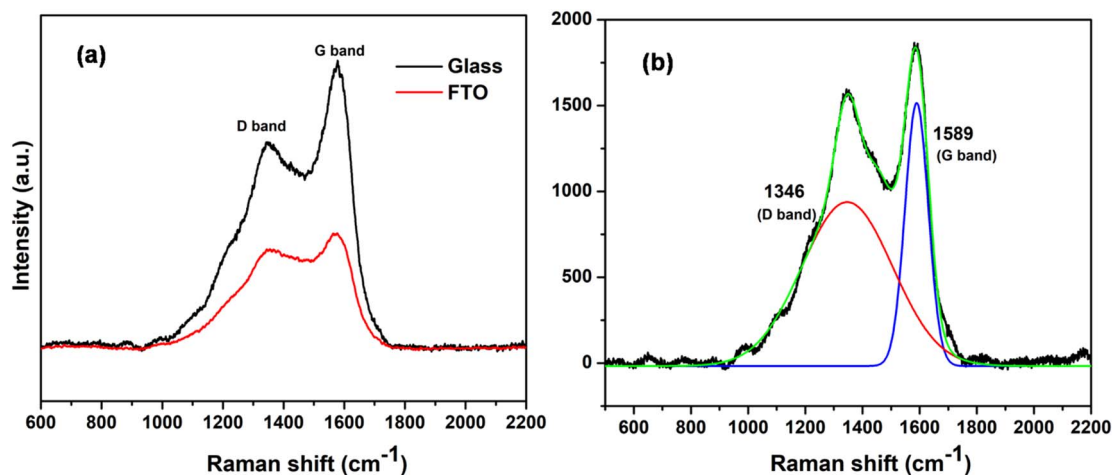


Figure 3. Raman spectrum of VCN thin film.

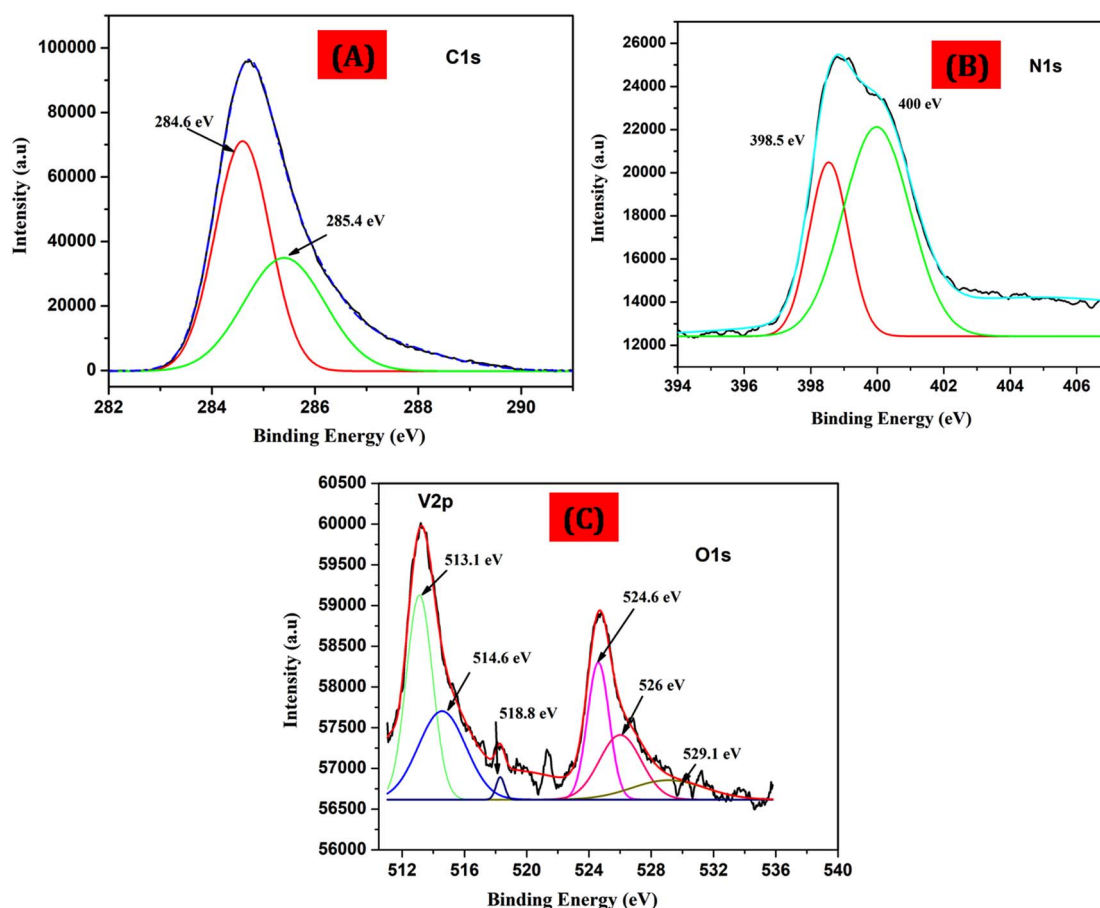
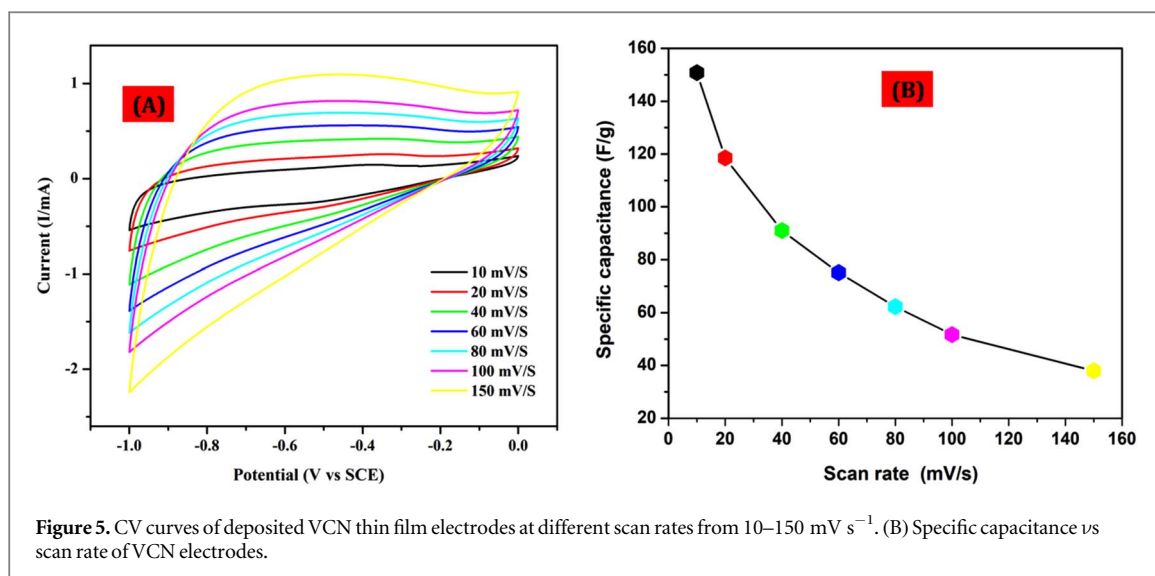


Figure 4. High-resolution XPS spectra of (A) C1s, (B) N1s, and (C) V2p & O1s of sputtered VCN thin film.

whereas Ag/AgCl and platinum rods were used as a reference and counter electrode, respectively. The cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) analyses of VCN thin films were carried out in a 2 M KOH electrolyte solution. Electrochemical impedance spectra (EIS) for both new and cycled electrodes were noted by supplying a 10 mV amplitude potential, and the spectra were recorded between the frequencies of 0.1 and 40 kHz. Cyclic voltammetric (CV) profiles were recorded in the ranges between -1.0 and 0 V versus Ag/AgCl. Figure 5(A) displays the CV profiles of VCN thin film. As seen in CV curves, the prepared VCN thin film electrodes exhibit anodic and cathodic peaks, which indicate a pseudo-capacitive that is the result of a fast, reversible faradic mechanism. Furthermore, with an



increasing scan rate, both the positions of the anodic and cathodic peaks shift towards positive and negative potential respectively due to the increment in the distance between the oxidation state and reduction state of metal oxide ions. Further, by increasing the scan rate, the CV closed curve area increased due to the fast redox kinetics occurring at the electrolyte and electrode interfaces [36].

The following formula is used to estimate the capacitance of the resultant thin film using the individual specific capacitance (C_s) of the active materials deposited onto the substrate [21]:

$$C_s = \frac{\int I dV}{vmV} \quad (1)$$

Here, I represents current (A), v represents potential scan rate (mV/s), m represents mass (active material), and V represents applied potential window (V). Figure 5(B) displays the computed specific capacitance as a function of the scan rate. The electrode showed a maximum C_s of 150 F g⁻¹ at 10 mV s⁻¹. The scan rate increased; the specific capacitance values reduced. This is correlated to the ion diffusion and electron kinetics within the electrode's active material. Also, because there is ample time to transport and diffuse OH⁻ ions into the entire electrode material, which enriches the particular capacitance, the electron transport and OH⁻ ion diffusion is high at low scan rates. On the other hand, the active material's comparatively insufficient electrochemical side, or faradic redox, makes it difficult for electrons and ions to penetrate at high scan rates. In order to comprehend how the working electrode behaves when operating at varied current rates, GCD characteristics were additionally studied. The GCD curve of the VCN thin film electrode is illustrated in figure 6 in the potential window range of -1.0–0 V at various current densities of 0.25–10 Ag⁻¹. The nonlinear charge–discharge curves in figure 6(A) further support the VCN thin film electrode's pseudo-capacitive behavior caused by the electrochemically reversible redox reaction of OH⁻ ions at the electrode–electrolyte interface.

Using the following formula, the C_s for the electrode material were evaluated from GCD graphs [21].

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (2)$$

Here, Δt - discharge time (s), and ΔV - discharge potential window (V).

The electrode showed a high specific capacitance of about 78.2 F g⁻¹ at a specific current density of 0.5 mA cm⁻². This indicates the good rate performance of the VCN thin film electrodes. The GCD curves are used to determine the specific capacitance values, and figure 6(B) depicts the related current density Versus specific capacitance plots. In these VCN thin films, the surface voids promote easy penetration of OH⁻ ions for maximum reversible redox route taking place at the electrode/ electrolyte interface. According to a number of studies on metal nitrides, the development of surface functional groups (oxides) upon this nitride surface triggers the redox reaction mechanism that results in energy storage [36]. According to XPS observations, the development of V-N-O on the surfaces of thin films results in the generation of vacancies (oxygen), which are in charge of pseudo-capacitive charge storage in these films [37, 38]. Moreover, it has been proposed that the vanadium oxynitride thin films have a partial metallic composition, which certainly explains why they have substantially better electrical conductivity [39].

Figure 7 displays the EIS spectra of VCN thin films prior to the cycle test. The smaller intrinsic resistance (R_s) and the smaller charge transfer resistance (R_{ct}) are obtained by the Nyquist plot of the VCN electrode with a

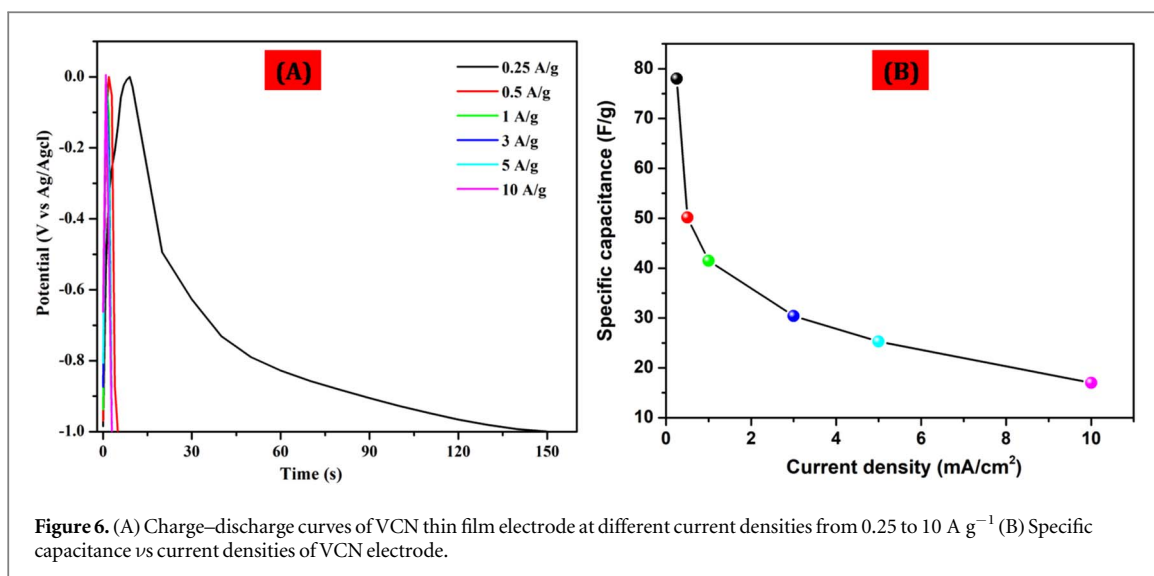


Figure 6. (A) Charge–discharge curves of VCN thin film electrode at different current densities from 0.25 to 10 A g^{−1} (B) Specific capacitance vs current densities of VCN electrode.

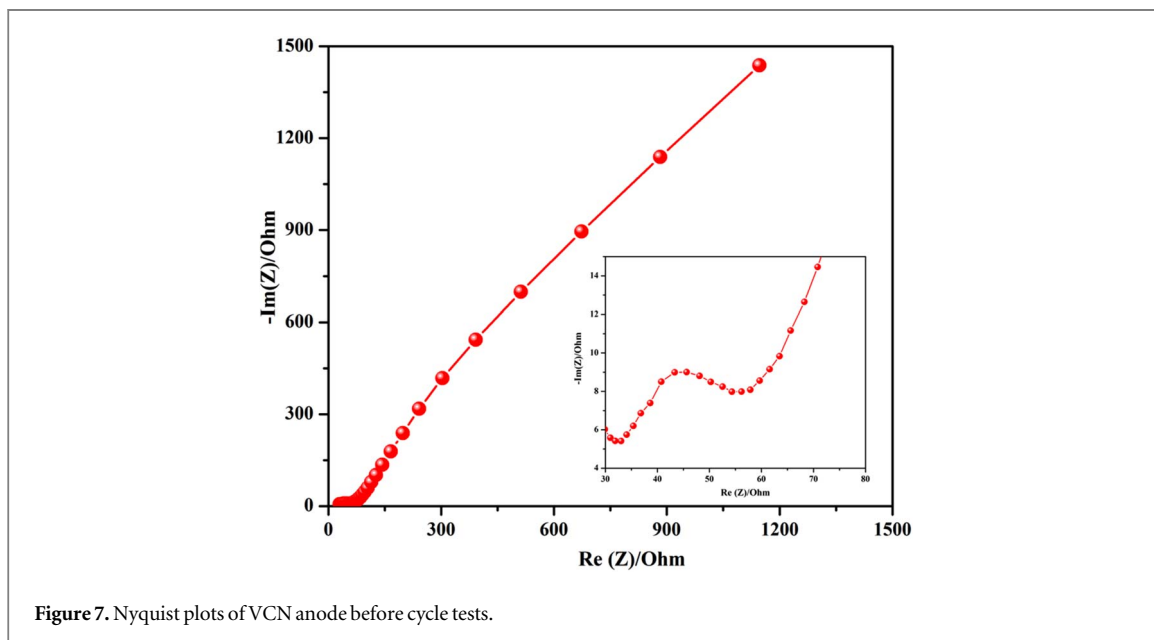


Figure 7. Nyquist plots of VCN anode before cycle tests.

steeper slope, a smaller intercept with the x-axis, and a smaller semicircle loop [38]. Before cycling responses, a semi-circular arc could be detected for VCN thin film. In the medium and high-frequency areas, a depressed semi-circle is seen for each curve, which is connected to the surface characteristics of thin film electrodes. These semicircles can be used to directly determine the charge transfer resistance, R_{ct} . The increase in R_{ct} values from 34.1 to 37.7 before the cycling reaction is a little different between the two curves. This variation in resistance could be due to the partial oxidation of the active nitride component [40]. The determination of long-cycle stability is a crucial factor in supercapacitor applications. We validated that the VCN electrode exhibits good electrochemical behavior based on the CV/GCD data. The cyclic stability was thus assessed. Figure 8(A) depicts the GCD cycles that were carried out at a current for the same density of 5 A g^{−1} in a 2 M KOH electrolyte. Along with having high electric conductivity and capacitance performance, the VCN electrode also has good cycling stability, retaining 87% of its capacitance at a current density of 5 A g^{−1} after 2000 cycles. In comparison, VCN exhibits excellent stability over 15000 cycles of testing, indicating that the VCN layer on its surface is beneficial for the cycling stability of the active electrode (figure 8(B)). Moreover, the fast-electrochemical process, which includes the fast faradaic reaction of V-C-N thin films and the ion adsorption/desorption of VCN, is linked to the capacitive contribution [41].

Figure 5(A) demonstrates that even at a high scan rate of 150 mV s^{−1}, the VCN electrode's CV curve retains its original shape, demonstrating the electrode's exceptional rate capacity. The VCN electrode's GCD curves (figure 6(A)) show a nearly symmetrical triangle when measured at different current densities (0.25–10 A g^{−1}), suggesting that the composite electrode has strong charge–discharge reversibility. Moreover, the VCN

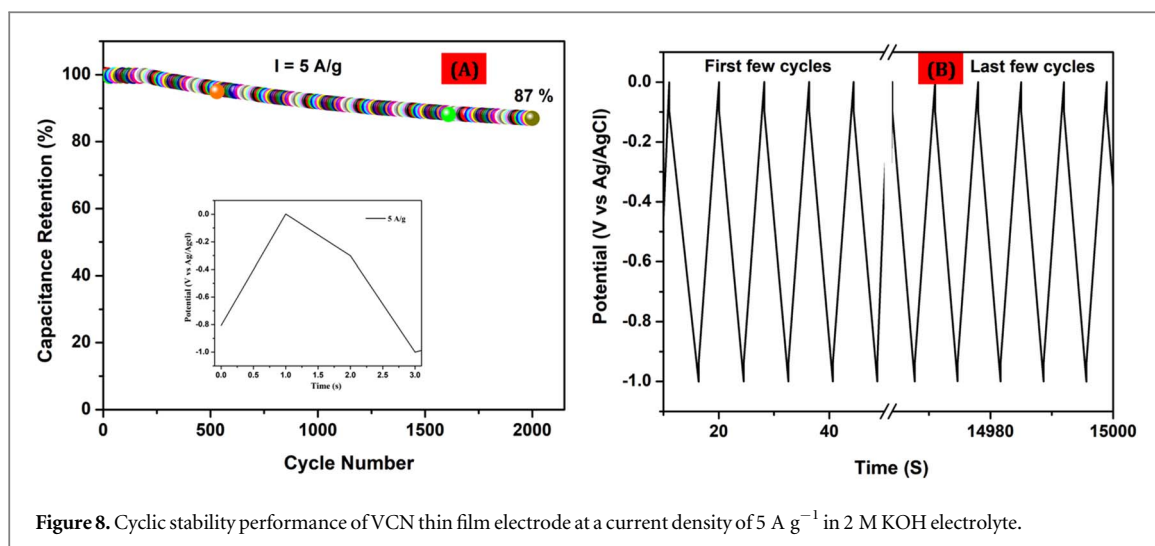


Figure 8. Cyclic stability performance of VCN thin film electrode at a current density of 5 A g^{-1} in 2 M KOH electrolyte.

Table 1. Comparison of the calculated specific capacitances in this work with other reports.

Active materials	Electrolyte	Specific capacitance (F g^{-1})	References
Vanadium nitride/Porous carbon	6 M KOH	52	[44]
VN/CNs composite	6 M KOH	78	[45]
VN/NCS	2 M KOH	76	[37]
VN/NCNT/NCN hybrids	6 M KOH	89	[46]
Passivated VN	0.1 M H_2SO_4	60	[47]
Sputtered VN thin Films	5 M KOH	47	[48]
VN/PCNPs	2 M KOH	43.5	
Nanostructured VN	1 M KOH	60	[49]
VN	2.0 M NaNO_3	45.7	[50]
Sputtered VCN Film	2 M KOH	78.2 F g^{-1}	Present work

electrode's coulombic efficiency at a current density of 5 A g^{-1} is 87%, indicating high electrochemical reversibility. The following factors may be responsible for the VCN composite's advantageous electrochemical characteristics: (I) More exposed VCN active sites are produced by vanadium carbon nitride dispersion, which results in excellent specific capacitance; (II) quaternary N and graphitic N in N-doped carbon are favorable for the improved performance of electrical conductivity for such electrode material [42, 43]; (III) mesoporous structure and a hollow cavity of VN/NC endow the composite electrode with more efficient electrolyte penetration and fast ion/electron transportation, resulting in improved electrochemical performance; (IV) the oxidation of VN is efficiently inhibited by a thin coating of NC on the surface of VN NPs, resulting in remarkable cycle stability. Figure 8(B) displays the charge–discharge curves for the initial and final few cycles. This feature, which is attributable to the thin VCN films, enhances electrolyte transport during the charge–discharge process and makes the electrode a good choice for pseudocapacitive applications. As a result, vanadium-based oxide and nitride are regarded as unique electrode materials that offer excellent energy as well as power densities for SCs. Also, as given in table 1, the observed results are superior than the reported values.

4. Conclusion

In conclusion, vanadium carbon nitride (VCN) thin films were successfully deposited on FTO substrates by pulsed DC magnetron sputtering technique for supercapacitor electrodes. The XRD study revealed the crystalline nature of VCN thin films. The morphological study from SEM and AFM discovered the smooth morphology of deposited film with an average grain size of 30 nm. Raman and XPS analysis confirmed the presence and formation of VCN thin films. The GCD study revealed a maximum Cs value of 78.2 F g^{-1} . EIS analysis reveals variations in charge transfer resistance that result from the partial oxidation of the active nitride component. The fabricated VCN electrode exhibited good cycling stability, retaining 87% of its capacitance at a current density of 5 A g^{-1} even after 2000 cycles. Thus, the fabricated VCN thin film is found to be a promising electrode for thin film supercapacitor devices.

Data availability statement

The datasets generated during the current study are available from the corresponding author on reasonable request. Compliance with Ethical Standards.

Contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by G V, J V, M S, and K S U. The first draft of the manuscript was written by G V, and J V K S U, P S, G B and G V, G R edited the entire draft. G V and G R supervised the whole work and edited the manuscript. All authors read and approved the final manuscript.

Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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