On the Capacities of Freestanding Vanadium Pentoxide–Carbon Nanotube–Nanocellulose Paper Electrodes for Charge Storage Applications

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1. Introduction

The demand on electrochemical energy storage devices, nowadays, is not only for operating our portable electronic devices and automobiles, but also for establishing stationary clean and sustainable energy resources.[1–4] For portable and wearable devices, the commercial interest is on the development of flexible and lightweight electrode materials with good rate performances, so that the electrodes can be charged rapidly.[5,6] Rechargeable batteries and supercapacitors are two categories of energy storage devices with different charge storage mechanisms. The charge storage mechanism in supercapacitors mainly originates from the charging of electric double layers (EDL), which yields high power densities but relatively low energy densities. The charge stored using the EDL mechanism is commonly reported in terms of specific capacitance with the unit F g⁻¹. Batteries, on the other hand, feature high energy densities but low power densities, as the full volume of the electrode material (and not only the electrode surface as in a supercapacitor) is assumed to be involved in the electrochemical reaction. The charge stored in battery-like materials is usually expressed in terms of specific capacity with the unit C g⁻¹ or mAh g⁻¹. Many studies have consequently been conducted to increase the energy densities of supercapacitors, including the use of nonaqueous electrolytes to expand the operating potential window,[4] and hybrid electrode materials consisting of both carbonaceous (double-layer charging) materials and redox active materials.[7]

The 2D transition metal oxides,[8–13] chalcogenides,[14,15] and carbides (MXenes)[16–19] are materials with promising properties compared with their bulk counterparts, including high aspect ratios, high ion diffusion rates between the layers, low electronic resistances, as well as good solution-based processabilities. Hydrated vanadium pentoxide (V_2O_5 ⋅ nH_2O) nanosheets are...
often assumed to be promising 2D materials based on the theoretical capacities of 965 or 1930 C g\(^{-1}\) calculated, assuming two or four electrons per V\(_2\)O\(_5\) unit (i.e., a complete reduction of V\(^{4+}\) to V\(^{2+}\) and V\(^{3+}\), respectively) and one water molecule per V\(_2\)O\(_5\) unit. The V\(_2\)O\(_5\) \(\cdot\) nH\(_2\)O nanosheet material is commonly composed of only a few layers, which has been reported to give a lithium-ion battery electrode capacity of 1728 C g\(^{-1}\) for 4 \(\mu\)m thick electrode at a current density of 10 mA g\(^{-1}\). The V\(_2\)O\(_5\) \(\cdot\) nH\(_2\)O interlayer distance (\(d\)-spacing) can vary between 6.34 and 13.80 Å, depending on the number of water molecules (\(n\)) present between the layers, which is why the double layer of V\(_2\)O\(_5\) \(\cdot\) nH\(_2\)O can host a variety of ions. It has been shown that V\(_2\)O\(_5\) \(\cdot\) nH\(_2\)O can be used as electrode materials for supercapacitors and rechargeable metal-ion batteries, e.g., lithium-ion batteries, sodium-ion batteries, magnesium-ion batteries, and zinc batteries. However, V\(_2\)O\(_5\) \(\cdot\) nH\(_2\)O electrodes generally exhibit low electronic conductivities and rapid capacity fading.

The latter capacity fading commonly stems from a combination of structural changes and dissolution of vanadium in the electrolyte, especially, in aqueous electrolytes. Many authors have, therefore, proposed possible solutions to the conductivity problem based on composite electrodes containing conducting polymers or carbon additives, such as graphene, carbon nanotubes (CNTs), or carbon dots. Likewise, some other nanostructured vanadium oxide and hydroxide materials were also encapsulated in carbonaceous network and showed good electrochemical performance.

A solid electrolyte has also been proposed to address the vanadium dissolution problem. Conventional cast electrodes, which contain organic binders and carbon black, on the other hand, typically suffer from problems such as decreased fractions of the electroactive compounds in the electrodes and slow diffusion of ions in the electrode. One promising approach is to use freestanding electrodes with relatively thin electroactive layers immobilized onto a porous fiber matrix with a large surface area as such electrodes should be less affected by the abovementioned problems.

The electrode dimensions and mass loadings are also important factors, which can influence the electrochemical behavior of the electrodes under investigation. In general, the use of electrodes with very small areas and, hence, very low mass loadings can lead to misleading conclusions about the electrochemical behavior (e.g., rate capability and long-term cycling) of a supercapacitor or battery material. The iR drop is, for example, directly proportional to the applied absolute current used, which depends on the amount of active materials (mass loading), whereas the electroactive material may not be fully accessible when using thick electrodes. When quite small electrodes are used, the iR drop will, hence, remain rather small even at high current densities. Significantly higher specific capacities are also expected for electrodes containing monolayers or only a few layers of the electroactive material in comparison with electrodes containing \(\mu\)m thick layers of the same material. This is a result of the much longer ion-diffusion lengths needed for the thicker electrodes, which imply that much longer times are needed to fully oxidize or reduce the thick electrodes. When comparing the performances of electrodes with different mass loadings, the capacity of the electrode (in, e.g., C or mAh) should, hence, also be considered. While monolayer-based electrodes often exhibit high specific capacities (e.g., in C g\(^{-1}\) of mAh g\(^{-1}\)), their capacities are generally too low to be of practical importance unless their mass loadings can be increased sufficiently without causing a significant decrease in their specific capacity. The mass loading of the electrode is likewise important when the active material undergoes dissolution in the electrolyte, because the capacity retention during long-term cycling then can depend on the dimensions and porosities of the electrodes. There is, therefore, a general need to study the influence of the electrode dimensions and mass loadings on the electrochemical behaviors of potential electrode materials.

Cellulose is a highly abundant sustainable material, which can be found in, e.g., trees, algae, and bacteria. As cellulose has many interesting properties, such as biodegradability, solution-based processability, high flexibility, and high mechanical strength, cellulose has been frequently used to fabricate electrode materials for wearable energy storage devices. This development has benefited significantly from access to straightforward manufacturing approaches. Wang et al. have, for example, described a straightforward vacuum filtration approach for the manufacturing of freestanding cellulose paper electrodes using a mixture of a redox active material, CNTs, and Cladophora cellulose (CC). As the latter electrodes are porous, high specific capacities as well as fast charge and discharge rates can be obtained when the thickness of the electroactive coating on the cellulose fibers and CNT fibers is thin enough (e.g., \(<50\) nm). Recently, this approach was also used in the manufacturing of nanostructured reduced molybdenum trioxide MoO\(_3\)\(\cdot\)\(\sim\)CNT–nanocellulose paper electrodes, which were found to show fast charge and discharge rates in supercapacitor applications (e.g., exhibiting the capacities of 30 C g\(^{-1}\) at a current density of 78 A g\(^{-1}\)). As it is reasonable to assume that this synthesis approach can also be used together with other solution-processable nanostructured materials, this possibility should, consequently, be further investigated.

Hydrated vanadium pentoxide (V\(_2\)O\(_5\) \(\cdot\) nH\(_2\)O, with \(n\approx1\)) nanosheets, composed of three to six layers, were recently prepared using water-based techniques and commercial vanadium oxide precursors. The synthesis involved a reflux of V\(_2\)O\(_5\) in hot water for 24 h in the presence of VO\(_2\) or oxalic acid, after which the formed nanostructured V\(_2\)O\(_5\) \(\cdot\) H\(_2\)O was collected using centrifugation and, subsequently, dried in air for a few hours. The process, which is efficient, fast, and provides a high yield, can be scaled-up to produce about 50 g. Drop-casting of an aqueous suspension of the nanosheet onto hydrophobic substrates, such as CNT paper, has been found to produce a surface layer of V\(_2\)O\(_5\) \(\cdot\) nH\(_2\)O on a CNT paper. Although V\(_2\)O\(_5\) \(\cdot\) nH\(_2\)O nanosheets have previously been used as electrode materials for lithium and sodium-ion batteries, the accessible capacity was found to depend on the electrode manufacturing method. There is, therefore, a need to explore the use of other hydrophilic substrates facilitating the attainment of a conformal distribution of the nanosheets. Furthermore, the electrochemical activity of the V\(_2\)O\(_5\) \(\cdot\) nH\(_2\)O nanosheets synthesized by aqueous exfoliation approach has not yet been explored in an aqueous electrolyte.

Herein, we describe a straightforward approach for the synthesis of freestanding V\(_2\)O\(_5\) \(\cdot\) H\(_2\)O–CNT–CC paper electrodes for energy storage applications in aqueous 1.0 m Na\(_2\)SO\(_4\) solutions.
The capacities of the electrodes are discussed based on the nature of the electrochemical reactions, the electrode mass loadings, and the distribution and thickness of the V$_2$O$_5$ · H$_2$O nanosheets in the electrode. The electrodes show promising rate capabilities and long-term cycling stabilities. Furthermore, a symmetric VO$_x$–CNT–CC energy storage device is tested and shown to exhibit a good capacity and rate capability within a potential window of about 1 V.

2. Results and Discussion

2.1. Synthesis and Morphology of the V$_2$O$_5$ · H$_2$O–CNT–CC Paper Electrodes

The V$_2$O$_5$ · H$_2$O nanosheets were prepared using water-based exfoliation of V$_2$O$_5$ in the presence of oxalic acid, and the chemical, thermal, and structural analyses of the obtained V$_2$O$_5$ · H$_2$O nanosheets have been described elsewhere. The as-prepared V$_2$O$_5$ · H$_2$O is composed of three to six layers and contains about 20% V$^{4+}$ as indicated by previous high resolution transmission electron microscopy, X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR), and X-ray absorption near-edge structure (XANES) data. Furthermore, previous findings indicate that there is approximately one water molecule per V$_2$O$_5$ unit at room temperature. The V$_2$O$_5$ · n H$_2$O–CNT–CC, hereafter denoted VO$_x$–CNT–CC, paper electrodes were prepared using a single step vacuum filtration method, as schematically shown in Figure 1. In a typical experiment, given amounts of V$_2$O$_5$ · nH$_2$O, CNTs, and CC in the weight ratios of 7:2:1 were dispersed by sonication in a 3:1 water–ethanol mixture. The formed suspension was then vacuum filtrated to form flexible and freestanding VO$_x$–CNT–CC paper. Figure 1d shows the as-prepared paper electrode in different bending states, reflecting the high flexibility of the VO$_x$–CNT–CC paper. The flexibility of the paper electrodes commonly increases the lifespan of the electrodes during long-term electrochemical cycling via decreasing the internal strain inside the electrodes. This good flexibility of the paper electrode can be attributed to the good mechanical properties of the cellulose nanofibers. The X-ray diffraction (XRD) pattern of the VO$_x$–CNT–CC paper (see Figure S1a, Supporting Information) shows that the structure of the V$_2$O$_5$ · H$_2$O within the cellulose paper electrodes is analogous to that of pristine V$_2$O$_5$ · H$_2$O.

Scanning electron microscopy (SEM) images of the VO$_x$–CNT–CC freestanding paper from side (cross section) and top views are shown in Figure 1e,f, respectively. The side view displays that the thickness of the cellulose paper electrode is about 20 μm, whereas the top view indicates that the V$_2$O$_5$ · H$_2$O is distributed within the randomly oriented CNT–CC matrix. Here, it should be noted that it is hard to distinguish between the CC fibers and the CNTs, as they have very similar morphologies. The energy-dispersive X-ray (EDX) mapping likewise indicates an even distribution of V, O, and C (see Figure S1b–e, Figure 1.

Figure 1. Synthesis and morphology of the VO$_x$–CNT–CC paper: a–c) schematic illustration of the synthesis method used to make the VO$_x$–CNT–CC freestanding paper. d) Photographs of the freestanding VO$_x$–CNT–CC paper showing its flexibility. e) Cross-sectional SEM image of the VO$_x$–CNT–CC paper. f) Top-view SEM image of the VO$_x$–CNT–CC paper featuring the distribution of V$_2$O$_5$ · H$_2$O within the CNT–CC matrix.
Supporting Information), further supporting a uniform distribution of V₂O₅·H₂O within the CNT–CC matrix. This finding is, however, challenged by the results of the electrochemical characterization, which indicates inhomogeneous depth distributions of V₂O₅·H₂O in the electrodes (see below). The latter indicates that some of the V₂O₅·H₂O was less electrochemically accessible even though a homogeneous distribution was seen in the EDX mapping results.

### 2.2. Electrochemical Behavior of the VOₓ−CNT–CC Paper Electrodes

The electrochemical behavior of the cellulose paper electrodes was investigated using cyclic voltammetry and constant current measurements. Figure 2a–c shows cyclic voltammograms (CVs) for the VOₓ−CNT–CC paper electrodes recorded at different scan rates. As indicated by the arrows in Figure 2a, the potential was initially scanned from the open circuit potential (OCP) of about 0.32 V down to −0.45 V and then back to 0.55 V. In some experiments, an extended potential window between −0.8 and 0.8 V was, however, also used. The OCP value suggests (see below) that the pristine VOₓ−CNT–CC electrodes contained mainly V⁺⁵ in agreement with previous XPS and NMR results for nanostructured V₂O₅·nH₂O.[11,13,20] The pristine electrodes showed an initial increase in the capacity during the first few cycles at a scan rate of 10 mV s⁻¹, indicating that the cycling opened up the structure and increased the interfacial surface area accessed by the electrolyte (see Figure 2a). The latter assumption was confirmed by electrochemical impedance spectroscopy (EIS) measurements on the cellulose paper electrodes prior (blue line) to and after 10 (red line) and 75 (black) electrochemical cycles, as a smaller charge-transfer resistance (Rᵣ) was obtained after the cycling (see the Nyquist plots in Figure 2g,h). Furthermore, the slope of the straight line in the low-frequency region of Nyquist plots increases by cycling, reflecting the increase in the ion transport rate during the electrochemical cycling.

The electrochemistry of vanadium-based electrodes in aqueous electrolytes is quite complicated due to the presence of several vanadium oxidation states. At pH 7, thermodynamic data[59,60] indicate that V₂O₅ (i.e., V⁺⁵), VO₂ (i.e., V⁺⁴), and V₂O₃ (i.e., V₊³) should be the dominating solid phases in the potential region of main interest here, i.e., −0.8 to 0.8 V versus Ag/AgCl (1 M KCl). The reduction reactions of interest here should, therefore, be the reduction of V⁺⁵ (i.e., V₂O₅) to V⁺⁴ (i.e., VO₂) and the reduction of V⁺⁴ (i.e., VO₂) to V₊³ (i.e., V₂O₃). These can be described using the reactions and standard reduction potentials [calculated using ΔG° = −nFE] presented in the following, which indicate that V₂O₅ should be stable at potentials above about 0.5 V versus Ag/AgCl (1 M KCl), whereas VO₂ should be found above 0.1 V versus Ag/AgCl (1 M KCl), assuming standard conditions (e.g., pH = 0).

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\begin{align*}
V_2O_5 + 2H^+ + 2e^- & \rightarrow 2VO_2 + H_2O & (1) \\
E' = 0.54 \text{ V versus Ag/AgCl (1 M KCl)} \\
2VO_2 + 2H^+ + 2e^- & \rightarrow V_2O_3 + H_2O & (2) \\
E' = 0.14 \text{ V versus Ag/AgCl (1 M KCl)}
\end{align*}
\]

Note also that both Reactions (1) and (2) should exhibit a pH dependence of ~59 mV pH⁻¹. The latter is important as measurements with pH indicator paper (see Figure S4e, Supporting Information) indicated that the pH in the electrolyte was roughly 4. This acidic pH can be explained by the presence of dissolved CO₂ and the low acid/base buffer capacity of the 1 M Na₂SO₄ electrolyte. At room temperature and normal pressure, the pH should be about 4 in a solution saturated with CO₂.[61] At pH 4, the equilibrium potentials should, consequently, be about 0.2 V more negative than the standard potentials (see Table S1, Supporting Information). This means that V₂O₅ should exist above about 0.3 V versus Ag/AgCl (1 M KCl), whereas VO₂ should be found above about −0.1 V versus Ag/AgCl (1 M KCl). The Pourbaix diagram[60] however, also suggests that the presence of soluble V⁺⁴² species may complicate the electrochemical behavior of the electrodes at potentials below about −0.6 V versus Ag/AgCl (1 M KCl) and pH < 4. Such a generation of soluble V⁺⁴² species should, however, only affect the electrochemical behavior of V₊³ in the extended potential region between −0.8 and 0.8 V versus Ag/AgCl (1 M KCl). As shown in Figure 2a, the couple redox peaks were clearly seen in the CVs obtained with the VOₓ−CNT–CC paper electrodes recorded using a scan rate of 10 mV s⁻¹. It is reasonable to assume that the redox pairs seen at about 0 and 0.17 V versus Ag/AgCl (1 M KCl), i.e., peaks 2 and 2', were due to the reduction of V₂O₅ (i.e., V₊³) to VO₂ (i.e., V⁺⁴) and the corresponding oxidation, respectively. The sharp redox peaks observed at about −0.246 V (peak 1, reduction) and −0.07 V (peak 1', oxidation) versus Ag/AgCl (1 M KCl) can analogously be assigned to the VO₂/V₂O₃ (i.e., V⁺⁴/V₊³) redox couple.

To explore the possibility of widening the potential window during electrochemical cycling of the cellulose paper electrodes, the performances of the electrodes were studied using different upper and lower cutoff potentials (see Figure 2b). When the potential window was expanded to cover −0.8 to 0.8 V versus Ag/AgCl (1 M KCl), the accessible capacity was increased (see Figure 2b, black curve). The reversibility of the system, however, decreased, as is shown by the increased coulombic efficiency values, especially at low scan rates (i.e., about 2 and 5 mV s⁻¹; see Figure S2a–c, Supporting Information). The reduction observed below −0.45 V versus Ag/AgCl (1 M KCl) was most likely due to hydrogen evolution, because the equilibrium potential for this reaction should be about −0.4 V versus Ag/AgCl (1 M KCl) at pH 4. It should be noted that the conversion of V₂O₅ to metallic vanadium (see Reaction (3)) is unlikely to influence the voltammogram as the equilibrium potential for this reaction should be about −0.64 V versus Ag/AgCl (1 M KCl) at pH 4. Moreover, V₂O₅ should not exist at −0.45 V versus Ag/AgCl (1 M KCl) due to its stepwise reduction to VO₂ and V₂O₃ during the cathodic scan. The reduction of V₂O₅ to VO₆[62] and metallic vanadium, respectively (see Reactions (4) and (5)) are also improbable based on their standard potentials of −0.65 and −0.90 V versus Ag/AgCl (1 M KCl) and their pH dependence of ~59 mV pH⁻¹ (see Table S1, Supporting Information), indicating that these reactions should take place outside the used potential window at pH 4.

\[
\begin{align*}
V_2O_3 + 10H^+ + 10e^- & \rightarrow 2V + 5H_2O & (3) \\
E' = -0.40 \text{ V versus Ag/AgCl (1 M KCl)}
\end{align*}
\]
Figure 2. Electrochemical performance of the VO\textsubscript{x}–CNT–CC paper electrodes: a) CVs showing the first (blue curve) and tenth (black curve) cycles at a scan rate of 10 mV s\textsuperscript{-1}. b) Third scan of CVs obtained at a scan rate of 2 mV s\textsuperscript{-1} using different upper and lower cutoff potentials. c) Third scan of CVs recorded using the scan rates of 2, 5, 10, and 20 mV s\textsuperscript{-1}. The arrows in (a–c) indicate the scan direction. d) The discharge (i.e., reduction) and charge (i.e., oxidation) capacities and the coulombic efficiency as a function of the logarithm of the scan rate. e) Potential versus capacity plots at the current densities of 1, 3, 5, 10, and 40 A g\textsuperscript{-1}. f) Potential versus capacity plots for the VO\textsubscript{x}–CNT–CC paper and CNT–CC paper at a current density of 1 A g\textsuperscript{-1}. The inset in (f) shows a schematic description of the cellulose paper electrodes. g,h) Nyquist plots for the pristine electrode (blue) and after 10 (red line) and 75 (black line) electrochemical cycles.
On the subsequent anodic scan, two main oxidation peaks are seen at about 0.15 and 0.65 V versus Ag/AgCl (1 M KCl) in Figure 2b. These oxidation peaks most likely correspond to the oxidation of $\text{V}^{5+}$ (i.e., $\text{V}_2\text{O}_3$) to $\text{V}^{6+}$ (i.e., $\text{VO}_2$) and $\text{V}^{7+}$ (i.e., $\text{V}_2\text{O}_4$), respectively. The increased oxidation charge compared with for cycling between −0.45 and 0.55 V versus Ag/AgCl (1 M KCl) (see the red voltammogram in Figure 2b) indicates that the generated hydrogen assisted in the reduction of the electrode, as indicated in Reactions (6) and (7). The more positive oxidation potentials seen for the black voltammogram compared with the red voltammogram in Figure 2b further indicate that the local pH at the electrode surface was increased due to the preceding hydrogen evolution.

Based on the electrochemical performance shown in Figure 2b, a potential window of −0.45 to 0.55 V versus Ag/AgCl (1 M KCl) was used in the cycling experiments discussed in the following. The results obtained with the $\text{VO}_x$-CNT-CC paper electrodes (see Figure 2d) indicated that the accessible capacity was almost approaching 200 C g$^{-1}$ at the scan rates of 2, 5, 10, and 20 mV s$^{-1}$. As the theoretical capacity of $\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$, assuming a complete reduction of $\text{V}_2\text{O}_5$ to $\text{V}_2\text{O}_3$ and one water molecule, is about 1930 C g$^{-1}$, it is immediately clear that the measured capacity of the $\text{VO}_x$-CNT-CC paper electrodes corresponded to about 10% of the theoretical capacity. This is, however, not unexpected as it is very unlikely that the theoretical capacity is reached experimentally, especially for this type of a two-step reduction process. As has been demonstrated for $\text{SnO}_2$ and $\text{Cu}_2\text{O}$ electrodes in Li-ion batteries,[63-65] both the oxide reaction and reformulation steps are rarely complete unless the oxide layer is very thin (on the order of nanometers). The reason for this is that a reduction of $\text{V}_2\text{O}_3$ to $\text{V}_2\text{O}_2$ should give rise to a passivating (i.e., reduced) $\text{VO}_2$ layer on top of the remaining $\text{V}_2\text{O}_3$ while a passivating oxide layer of $\text{V}_2\text{O}_3$ would be formed on top of the $\text{VO}_3$ during the subsequent oxidation step. In the $\text{V}_2\text{O}_3$ case, this effect (which incidentally should result in broader reduction and oxidation peaks) should appear both during the $\text{V}_2\text{O}_3$ and $\text{VO}_2$ reduction and oxidation steps. After the first reduction scan, there could, hence, be a layer of $\text{V}_2\text{O}_3$ on top of a layer of $\text{VO}_2$ on top of a layer of the pristine $\text{V}_2\text{O}_3$ if the $\text{V}_2\text{O}_3$ layer was too thick to be completely reduced during the scan prior to the onset of the reduction of $\text{VO}_2$ to $\text{V}_2\text{O}_3$. Analogously, a layer of $\text{V}_2\text{O}_3$ on top of a layer of $\text{VO}_2$ on top of any remaining $\text{V}_2\text{O}_3$ (on top of any $\text{VO}_2$ and $\text{V}_2\text{O}_3$ still present after the reduction step) would be expected to be found after the first oxidation cycle. As is indicated in Reaction (1) and (2), $\text{H}^+$ would need to diffuse from the solution and into the material during the reduction steps and out toward the solution during the oxidation steps to maintain charge neutrality in the material. As a result of the diffusion-controlled reactions, the shapes of the voltammograms (particularly at higher scan rates) become analogous to those of voltammograms obtained with supercapacitor electrodes (i.e., EDL charge storage mechanism). This fact incidentally explains why capacitances (expressed in F g$^{-1}$) rather than capacities (expressed in C g$^{-1}$ or mAh g$^{-1}$) are often reported for vanadium oxide-based electrodes in conjunction with energy storage devices. In the present case, the currents are, however, clearly due to redox reactions with inherent specific redox potentials, although the peaks become more and more drawn out as a result of the diffusion-controlled processes discussed earlier. This, consequently, means that the capacity (or capacitance) will be strongly dependent on the thickness of the $\text{V}_2\text{O}_3 \cdot \text{H}_2\text{O}$ nanosheets and the time scale of the experiments. A restacking of the $\text{V}_2\text{O}_3 \cdot \text{H}_2\text{O}$ nanosheets to form thicker layers, hence creating long diffusion paths in the oxide layers, cannot be excluded. The present results, consequently, indicate that the relatively low capacity was due to the fact that mainly the surface of the $\text{VO}_x$-CNT-CC material was electrochemically active (see inset in Figure 2f), and that the specific capacity should decrease when the thickness of the $\text{V}_2\text{O}_3 \cdot \text{H}_2\text{O}$ nanosheets is increased. Results obtained with an electrode coated with a thin nanosheet layer should, hence, only be used to predict the capacity of an electrode with a mass loading of mg cm$^{-2}$ if a restacking of the layers can be prevented during the upscaling of the electrode mass loading.

The mass loading of the electrode should also affect the iR (i.e., the ohmic) drop in the electrodes as the currents obtained in the voltammograms, or used in the constant current experiments, should increase when increasing the mass loading. If the iR drop is increased, the capacity should decrease as a result of a decrease in the width of the potential window as the potential or cutoff limits would be reached prematurely. Interestingly, the peak-to-peak separations did not increase significantly when increasing the scan rate from 2 to 20 mV s$^{-1}$ (see Figure 2c). However, when higher scan rates were used (i.e., 50-500 mV s$^{-1}$), the capacity decreased with increasing rate (see Figure 2d), and the voltammograms also became significantly distorted (see Figure 2b, Supporting Information) due to the increased iR drop. Voltammograms with analogous shapes were also obtained when the potential window was expanded from −0.8 to 0.8 V versus Ag/AgCl (1 M KCl) (see Figure 2b, Supporting Information). The coulombic efficiency was about 95% at the low rates (due to the increased chance of the slow parasitic reactions such as H$_2$ evolution) and 100% at the high rates, indicating a high reversibility of the redox reactions. This is in a good agreement with previous findings for the abovementioned SnO$_2$ electrodes[63-65] for which a steady-state situation was seen to develop as the initially larger reduction charge gradually decreased to finally match the oxidation charge even though the obtained capacity was significantly lower than the theoretical capacity.

Galvanostatic charge–discharge experiments were likewise conducted in the potential window between −0.45 and 0.55 V versus Ag/AgCl (1 M KCl). Overall, the galvanostatic results were analogous to the cyclic voltammetric results. The sloping reduction (i.e., discharge) curves shown in Figure 2e, as well as the broad voltammetric peaks in Figure 2c, can be explained by the poor crystallinity of the $\text{V}_2\text{O}_3 \cdot \text{H}_2\text{O}$ nanosheets, reflected in the XRD pattern (see Figure S1a, Supporting Information) featuring only broad 00l peaks.[11,20,23] The reduction (discharge)
capacities were about 250, 200, 170, 136, and 44 C g\(^{-1}\) with the current densities of about 1, 3, 5, 10, and 40 A g\(^{-1}\). These values are comparable to those obtained in the voltammetric experiments even though a strict comparison is difficult to carry out, because the effective reduction time in the voltammetric case depended on the reduction onset potential. The capacity retention observed at high rates (i.e., 5–40 A g\(^{-1}\)), which ranged between 70% and 20%, was comparable to that obtained in the voltammetric experiment (see Figure 2d). It was also found that the contribution of the CNTs to the measured capacity was about 20 C g\(^{-1}\) compared with the 250 C g\(^{-1}\) obtained with the VO\(_x\)-CNT–CC electrodes at a current density of 1 A g\(^{-1}\) (see Figure 2f). This demonstrates that the major part of the capacity stemmed from the V\(_2\)O\(_5\)-H\(_2\)O nanosheets. This is in a good agreement with the corresponding comparison of the voltammetric behaviors of the VO\(_x\)-CNT–CC and CNT–CC electrodes shown in Figure S2e,f, Supporting Information. The observed redox peaks at about 0.36 and 0.45 V versus Ag/AgCl (1 M KCl) can, most likely, be explained by surface confined reduction and oxidation of the CNT surfaces, respectively. These CNT redox peaks cannot be observed in the VO\(_x\)-CNT–CC voltammograms due to the larger the current originating from the V\(_2\)O\(_5\)-H\(_2\)O. A comparison of the results obtained with the present VO\(_x\)-CNT–CC electrodes and other V\(_2\)O\(_5\)-based electrodes is presented in Table S2, Supporting Information. The latter illustrates the good rate performance and long-term cycling stability of the present cellulose paper electrodes as well as the high specific capacity that could be obtained despite the use of a mass loading of about 2 mg cm\(^{-2}\).

2.3. Insights Regarding the Long-Term Cycling of the VO\(_x\)-CNT–CC Paper Electrodes

To explore the factors affecting the electrochemical behavior of the VO\(_x\)-CNT–CC electrode during long-term cycling as well as the reproducibility of these results, experiments were conducted using three electrodes with the same size and mass loading (i.e., 0.32 cm\(^2\), 650 μg), and the detailed experiments are summarized and discussed in Note S1, Supporting Information, and Figure S3 and S4. The results showed that the capacity retention of VO\(_x\)-CNT–CC electrodes varied between 85% and 46% after 8000 cycles. This wide range may be attributed to a difference in the concentration of V\(_2\)O\(_5\)-H\(_2\)O close to the surface of the different electrodes (see CVs in Figure S3a, Supporting Information). Another possibility is that the thicknesses of the V\(_2\)O\(_5\)-H\(_2\)O layers were not the same everywhere in the three electrodes, e.g., due to different degrees of restacking, even though their mass loadings were very similar. As the V\(_2\)O\(_5\)-H\(_2\)O nanosheets most likely were thinner and/or located closer to the surface of the electrodes with fast fading, therefore, the difference in the capacity retention is unlikely to have been due to the electrochemical cycling effects involving the formation of passivating oxide layers discussed earlier. This suggests that the capacity losses were more likely to have been caused by vanadium oxide dissolution in the electrolyte, further motivated in Note S1, Supporting Information.

One way to reduce a fading capacity could be to use a surface coating, which is able to slow down the vanadium dissolution rate while not obstructing the diffusion of the charge compensating protons. MXenes are promising 2D materials, which can exhibit high conductivities and capacitances, which, in turn, make them good candidates for use as surface coatings on the VO\(_x\)-CNT–CC paper electrodes. Therefore, Mo\(_{1.33}\)C MXene surface coatings (containing 80 μg cm\(^{-2}\), implying a thickness of about 120 nm based on a density of Mo\(_{1.33}\)C\(^{[47]}\) of 3.4 g cm\(^{-3}\)) were here deposited on VO\(_x\)-CNT–CC electrodes by drop-casting an MXene aqueous suspension (0.7–1.0 mg mL\(^{-1}\)) on both sides of the electrodes; see SEM and EDX mapping in Figure S5, Supporting Information. The electrodes were first dried in air for 30–60 min, at room temperature, after which they were stored in an inert argon atmosphere. This MXene-coating approach did, however, not result in a significantly improved long-term cycling performance as analogous capacity losses were also seen for the Mo\(_{1.33}\)C-coated electrodes (see Figure S6, Supporting Information).

2.4. Influence of the Mass Loading on the Rate Capability and Long-Term Cycling Stability

The performance of electrodes with different dimensions and mass loadings was also compared using three electrodes referred to as large (0.50 cm\(^2\), 950 μg), moderate (0.32 cm\(^2\), 650 μg), and small (0.08 cm\(^2\), 150–240 μg), and schematically described in Figure 3a. As shown in Figure 3b, the CVs for the large and small electrodes shared similar overall shapes even though the sharper peaks seen for the small electrode indicated a higher surface concentration of the V\(_2\)O\(_5\)-H\(_2\)O nanosheets. The shifts in the peak potentials as well as the distortions of the voltammograms shown in Figure 3b,c with increasing the scan rate can be explained by the increased iR drop.

As expected, the capacity depended on the mass loading of the electrode (see Figure 3d), indicating that the electroactive fraction of the V\(_2\)O\(_5\)-H\(_2\)O nanosheets was about the same in the large and small electrodes. The capacity retentions at 500 mV s\(^{-1}\) were also analogous, i.e., 25% and 28% of the capacity at 2 mV s\(^{-1}\) for the large and small electrode, respectively. The latter indicates that the capacity losses seen at high scan rates mainly were a result of the diffusion limited redox reactions, although the iR drop also gave rise to smaller active potential windows and, hence, smaller capacities. The larger specific capacity seen for the small electrode compared with that of the large one at the lowest scan rates can most likely be explained by the abovementioned differences between the surface concentrations of the V\(_2\)O\(_5\)-H\(_2\)O nanosheets. The latter hypothesis is supported by the fact that the rate dependences of the moderate and large electrodes (see Figure 3e) did not differ significantly.

While the large electrode showed a capacity retention of about 80% (see Figure S7a, Supporting Information) during 5000 cycles at a current density of about 10 A g\(^{-1}\), a capacity retention of about 25% was obtained for the small electrode after 1000 cycles at a current density of 1 or 6.25 A g\(^{-1}\) (see Figure S7b,c, Supporting Information). This difference was most likely a result of the previously mentioned formation of dissolvable vanadium species and the higher surface concentration of the V\(_2\)O\(_5\)-H\(_2\)O nanosheets for the small electrode. The influence of the latter effect was also enhanced by the lower amount of active material in the small electrode (i.e., 150–240 μg) as this
should decrease the likelihood of obtaining a saturated solution in the vicinity of the electrode. The initial increase in the capacity seen for the small electrode in Figure S7c, Supporting Information, was probably caused by a gradual wetting of the electrode yielding an increasing electrode area. All in all, the optimum loadings and dimensions of the electrodes will depend on the final use of the charge storage device; however, they should be considered carefully during the interpretation of the electrochemical behavior.

2.5. Electrochemical Performance of VOₓ–CNT–CC Paper Electrodes Symmetric Device

To investigate the performance of the V₂O₅⋅H₂O–CNT–CC paper electrodes in an energy storage device, a symmetric two-electrode device was assembled and cycled over a cell voltage window of 1 V. As seen from the obtained CVs recorded at different scan rates and displayed in Figure 4a,b, the behavior of the device was analogous to that seen for a supercapacitor, which is why both the specific electrode capacities and capacitances have been reported in Table S2, Supporting Information. Here, it should be pointed out that the mass loadings used in the experiment should be considered when comparing different values as very high specific capacities or capacitances can be obtained using electrodes with very low mass loadings even though the capacities or capacitances of such electrodes would be too small to be of any practical interest. The device capacities were about 50 mC (40 C g⁻¹) and 12 mC (10 C g⁻¹) at the scan rates of about 2 and 1000 mV s⁻¹, respectively (see Figure 4e) after normalization using the masses of the active materials in both two electrodes. In agreement with the voltammetric results, the constant
current measurements gave rise to sloping charge–discharge profiles, as shown in Figure 4c. The device capacity evaluated from the latter curves was about 40 mC (34 C g\(^{-1}\)) and 13 mC (11 C g\(^{-1}\)) using the current densities of about 0.5 and 10 A g\(^{-1}\), respectively (see Figure 4f). The low normalized device capacities compared with the theoretical capacity of about 480 C g\(^{-1}\) can be attributed to the diffusion limitations associated with the redox reactions discussed earlier. The long-term cycling of the symmetric device showed (see Figure 4d) that the capacity retentions after 1000 and 2000 cycles were of about 86% and 60%, respectively. As discussed earlier, this decrease in the capacity retention can be explained by vanadium species undergoing dissolution in the electrolyte. Despite this, the coulombic efficiency remained close to 100% during 2000 cycles, reflecting the high reversibility of the electroactive parts of the electrodes. It can, consequently, be concluded that the coulombic efficiency constitutes a rather blunt instrument when evaluating the performance of this type of energy storage devices.

3. Conclusion
A straightforward and novel approach for fabricating vanadium oxide-based electrodes (VO\(_x\)-CNT–CC), using a porous CNT–CC matrix, was described for use in aqueous energy storage devices. The VO\(_x\)-CNT–CC electrodes with the mass loadings of about...
2 mg cm\(^{-2}\) exhibited the capacities of about 250 and 44 C g\(^{-1}\) in 1 M Na\(_2\)SO\(_4\) at the current densities of about 1 and 40 A g\(^{-1}\), respectively. The long-term cycling of the electrodes was influenced by a dissolution of vanadium species in the electrolyte; consequently, the capacity retention varied between 46\% and 85\% after 8000 cycles, depending on the thickness of the V\(_2\)O\(_5\) \cdot H\(_2\)O layer and/or the V\(_2\)O\(_5\) \cdot H\(_2\)O concentration at the surface of the V\(_2\)O\(_5\)-CNT-CC electrodes. The use of thin coating of Mo\(_{0.15}\)C MXene applied on the surface of the VO\(_x\)-CNT-CC electrodes was also investigated; however, it did not efficiently minimize the dissolution. The vanadium oxide was well distributed within the matrix as a whole; however, variations in the depth distribution and the thickness of the V\(_2\)O\(_5\) \cdot H\(_2\)O nanosheets influenced the electrochemical results significantly due to the accessible capacity being determined by diffusion controlled redox reactions involving the reduction of V\(_2\)O\(_5\) to VO\(_2\) and VO\(_2\) to V\(_2\)O\(_3\). A symmetric device containing two VO\(_x\)-CNT-CC paper electrodes was found to exhibit a capacity of 40 C g\(^{-1}\) at a scan rate of 2 mV s\(^{-1}\), which can be attributed to the surface of the electrode being electrochemically active as a result of diffusion limitations. To realize the full potential of these materials, further studies are needed to develop approaches for immobilizing nanometer thin layers of vanadium oxide (e.g., vanadium oxide nanosheets) on porous, flexible, and conducting substrates, and to prevent possible restacking of the vanadium oxide nanosheets used herein during the electrode fabrication.

4. Experimental Section

**Synthesis of Nanostructured V\(_2\)O\(_5\)-nH\(_2\)O and VO\(_x\)-CNT-CC Paper Electrodes:** V\(_2\)O\(_5\) (1 mmol, i.e., 0.182 g) (Beijing chemical reagent industry) was dispersed in deionized water by sonication for 10 min, after which 0.5 mmol (i.e., 0.630 g) of oxalic acid, H\(_2\)C\(_2\)O\(_4\) \cdot 2H\(_2\)O (Xilong chemical Ltd.), was added. The suspension was purged with argon for 5 min and stirred under reflux at 80 °C for 24 h. The resulting black-greenish suspension of V\(_2\)O\(_5\)-nH\(_2\)O was dried at 60 °C for 10 h to obtain the nanostructured V\(_2\)O\(_5\)-nH\(_2\)O (with n ∼1 at 25 °C). The synthesis process was robust and could be scaled-up to yield 10 g.\(^{[57]}\)

The paper electrodes were fabricated similar to the previously reported protocol.\(^{[51,52,56]}\) In particular, 70 mg of V\(_2\)O\(_5\)-nH\(_2\)O nanosheet powder, 20 mg of multi-walled CNTs, and 10 mg of CC were dispersed in a water-ethanol mixture (60 mL of water and 20 mL of ethanol) and sonicated for 20 min. The formed mixture was filtered under vacuum on a polypyrrole filter to produce a paper sheet. The paper sheet was allowed to dry at room temperature and then peeled off the polypyrrole filter yielding a freestanding paper electrode. The overall loading including the nanocellulose was about 2 mg cm\(^{-2}\), and active mass loading (mass of V\(_2\)O\(_5\)-nH\(_2\)O and CNTs) was about 1.8 mg cm\(^{-2}\). Similarly, the CNT-CC paper electrodes were synthesized using a mixture of CNT and CC of 1:1 weight ratio.

**Material Characterization and Electrochemical Measurements:** All electrochemical experiments were performed in a stainless-steel Swagelok cell. Gold foil was used as a current collector, whereas a piece of Celgard 2501 soaked in 1.0 M Na\(_2\)SO\(_4\) (500 μL) was used as the separator. Cyclic voltammetry and galvanostatic charge-discharge experiments were used to examine the electrochemical behavior of the VO\(_x\)-CNT-CC paper electrodes. In the three-electrode experiments, the VO\(_x\)-CNT-CC paper electrodes were used as the working electrodes, whereas a circular piece of activated carbon (8 mm diameter, with a mass loading of 5–8 mg, YP-50, Kuraray, Japan) was used as the counter electrode, and a Ag/AgCl (1 M KCl) electrode was used as the reference electrode. The potential was generally scanned between −0.45 and 0.55 V versus Ag/AgCl (1 M KCl), but some experiments were also conducted in the potential window −0.8 to 0.8 V versus Ag/AgCl (1 M KCl). The overall working electrode mass was varied between 150 and 950 μg, and the capacity was normalized with respect to the VO\(_x\)-CNT mass (i.e., 90% of the total electrode mass). The working electrodes had the diameters of about 8.0 mm corresponding to an area of about 0.5 cm\(^2\) (large electrode) and 6.4 mm corresponding to an area of about 0.32 cm\(^2\) (moderate electrode). Some experiments were also done using rectangular electrodes with the dimensions of 2–3 mm corresponding to an area of about 0.08 cm\(^2\) (small electrode).

The two-electrode symmetric device experiments were done using a couple of symmetric circular (6.4 mm diameter) VO\(_x\)-CNT-CC paper electrodes. The total dry mass of each electrode (prior to the assembly of the device) was about 650 μg, and the mass normalization was done with respect to total the active mass of the two electrodes (i.e., \(2 \times 650 \times 0.9\) μg). Cyclic voltammetry and constant current experiments were used to explore the electrochemical performances of the symmetric devices for cell voltages between 0.0 and 1.0 V.

The standard potentials indicated in association with the reactions given as follows were calculated based on the change in Δ\(G^0\), using Δ\(G^0 = −nFE^0\) and published Δ\(G^0\) values.\(^{[67]}\)

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

carbon nanotubes, cellulose nanofibers, energy storage, freestanding paper electrodes, vanadium oxide nanosheets

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