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Flexible Freestanding MoO_{3-x}-CNTs-Nanocellulose Paper Electrodes for Charge Storage Applications

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Abstract

Herein, we report a one-step synthesis protocol for synthesizing freestanding/flexible paper electrodes composed of nanostructured molybdenum oxide (MoO_{3-x}) embedded in a carbon nanotubes (CNTs) and *Cladophora* Cellulose (CC) matrix. The preparation method involves sonication of the precursors, nanostructured MoO_{3-x}, CNTs, and CC with weight ratios of 7:2:1, in a water-ethanol mixture, followed by vacuum filtration. The electrodes are straightforward to handle and possess a thickness of about 12 μm and a mass loading of MoO_{3-x}-CNTs of about 0.9 mg cm^{-2} . The elemental mapping shows that the nanostructured MoO_{3-x} is uniformly embedded inside the CNTs-CC matrix. The MoO_{3-x}-CNTs-CC paper electrodes feature a capacity of 30 C g^{-1} , normalized to the mass of MoO_{3-x}-CNTs, at a current density of 78 A g^{-1} (corresponding to a rate of about 210 C based on the MoO₃ content, assuming a theoretical capacity of 1339 C g^{-1}), and exhibit a capacity retention of 91% over 30 000 cycles. This study paves the way for the manufacturing of flexible/freestanding nanostructured MoO_{3-x} based electrodes for use in charge storage devices at high charge-discharge rates.

1. Introduction

Nowadays, charge storage devices are widely used in many applications including portable devices, wearable electronics, and electric vehicles^[1–3]. These applications require the electrode materials to be lightweight, and to exhibit high flexibilities and good high rate performances so that the electrodes can be charged rapidly. In general, electrochemical charge storage devices can store charge based on two different mechanisms, where the first mechanism involves storing the charge at the electrode/electrolyte interfaces in electrochemical double layer capacitors (EDLCs).^[4] These EDLCs typically employ carbonaceous electrode materials with high surface areas,^[5,6] as the charge storing capacities depend on the electrochemically active area of these electrodes. The second mechanism, in which the charge storage results from electrochemical reactions involving the electrode materials, can involve a range of materials such as electronically conductive polymers and transition metal oxides.^[7–10] Compared to the carbonaceous electrodes, the electrochemically active electrodes generally exhibit higher energy densities but also often require lower charge and discharge rates as a result of the fact that the entire volume of the electrode then can be employed (compared to only the electrode surface in the double layer capacitance case). Many researchers have therefore focused on the preparation of hybrid electrode materials, composed of thin layers of electroactive materials coated on substrates with large surface areas, to obtain high capacities as well as high charge and discharge rate capabilities.^[10,11]

Cellulose is a sustainable and biodegradable material, as well as the most abundant natural polymer, and it can be extracted from e.g. wood, algae and bacteria.^[10,12–16] Cellulose can be used in many applications, including water purification, fire-retardants, and paper manufacturing.^[13,14] In the last few years, nanocellulose has been used to fabricate paper-based flexible electrodes for energy storage applications, due to its resource abundance, high mechanical flexibility and excellent solution processability.^[10,16–22] While many methods have been used to prepare paper-based electrodes, including printing methods, vaporization methods, and vacuum filtration methods,^[17,22] Wang et al.^[23,24] recently introduced a robust synthesis protocol for the manufacturing of flexible freestanding paper electrodes using a combination of a redox active material, carbon nanotubes (CNTs), and *Cladophora* Cellulose (CC). Therefore, there is a need to explore the extension of the aforementioned synthesis approach to

include some other redox active materials such as transition metal oxides nanosheets, e.g. vanadium^[25–27] or molybdenum oxide nanosheets.^[28,29]

Molybdenum oxides have previously been used in a variety of electrochemical applications such as electrode materials for lithium-ion batteries, sodium-ion batteries, and supercapacitors.^[30–35] However, molybdenum oxide based electrodes usually suffer from low electronic conductivities, fast capacity fading and poor electrochemical cyclabilities.^[36] So far, many modifications were described in literature in order to improve the performance of the molybdenum oxides based electrodes, for example some studies showed that the use of reduced molybdenum oxides (MoO_{3-x}) rather than MoO_3 can increase the pseudocapacitance of the electrodes.^[37] In the meantime, the inclusion of conductive additives such as graphene^[11] or carbon nanotubes^[34,38] was shown to enhance the electrochemical behavior of the molybdenum oxide electrodes. On the other hand, the conventional electrode fabrication method commonly involved the use of organic binder which can influence the electrochemical behavior of the electrodes, for example reducing the accessible capacity and long-term cycling stability.^[38] Recently, L. Huang et al.^[39] and B. Yao et al.^[35] reported synthesis protocols for fabricating free-standing MoO_3 nanopapers to overcome on the use of organic binder. Likewise, freestanding electrodes were also fabricated by drop cast a dispersion of the molybdenum oxide onto a conductive substrate.^[28]

Recently, we reported on the use of freestanding electrodes of reduced molybdenum trioxide (MoO_{3-x}) nanosheets deposited onto carbon paper for charge storage application;^[28,40] which showed good electrochemical performance when used in electrodes in which the thickness of the active material was limited to about 4 to 5 μm . The limited thickness of active material meant that the capacities of the electrodes were relatively low and as the electrodes also could be cycled for only about 2000 cycles, it was immediately clear that another electrode manufacturing approach would be required to allow this type of electrodes be used in energy storage devices, i.e. a method which enables the increase of the active material thickness and stabilizes the long-term cycling. One approach to increase the performance of these electrodes could be to mix the molybdenum trioxide with a conductive additive such as a carbonaceous material (e.g. graphene or CNTs),^[32,33,41] and nanocellulose to yield flexible and

freestanding paper electrodes using the approach recently employed to make conductive nanofiber networks composed of CNTs and nanocellulose.^[23,24]

The present work describes a straightforward approach for the manufacturing of porous, freestanding and flexible electrodes composed of MoO_{3-x} -CNTs-CC, in which the CC serves as a dispersing agent and flexible substrate, while the CNTs act as a conductive additive. The electrodes are tested in 1.0 M H_2SO_4 and cycled between 0 and 0.5 V vs. Ag/AgCl (1 M KCl). The mass of the electrodes was between 0.10 and 0.21 mg, and their lateral dimensions were about 2 to 3 mm. The capacity was normalized to the mass of MoO_{3-x} -CNTs, which corresponded to about 90% of the electrode mass.

2. Results and discussion:

Paper-based electrodes have recently attracted a lot of attention due to e.g. their applicability in conjunction with wearable electronics. In this study, the MoO_{3-x} -CNTs-CC paper electrodes were prepared using a straightforward one-step vacuum filtration method. A mixture of MoO_{3-x} nanosheets (prepared using a previously described water-based exfoliation technique),^[28] CNTs, and CC in weight ratios of 7:2:1 was first dispersed in a 3:1 water-ethanol mixture, after which the suspension was filtrated under vacuum to yield a freestanding paper electrode. Figure 1a displays a schematic illustration of the fabrication of the MoO_{3-x} -CNTs-CC paper electrode. It worth mentioning that the detailed structural and morphological characterizations of the MoO_{3-x} precursor were described in a previous report.^[28]

The XRD pattern of the obtained MoO_{3-x} -CNTs-CC paper (see Fig. S1a) indicated that the material was close to amorphous and that the degree of the crystallinity of the MoO_{3-x} nanosheets hence was low, in good agreement with previous findings.^[28,29] The peak observed at 14.5° can be assigned to the CNTs-CC matrix, since it was also observed in the XRD pattern of the CNTs-CC paper. Interestingly, the MoO_{3-x} -CNTs-CC paper electrodes featured an electronic conductivity of about 0.019 S cm^{-1} , as determined using four-point probe measurements. This electronic conductivity value shows that the electrical properties of the present MoO_{3-x} -CNTs-CC paper were comparable to those of previously

described MoO_3 based nano-paper electrodes.^[35,39] In addition, the MoO_{3-x} -CNTs-CC paper electrodes were highly flexible as shown in Fig. 1b. The flexibility was confirmed via measurements of its Young's modulus using nanoindentation tests, yielding a value of about 5.3 ± 0.6 GPa (see Fig. S1). The high flexibility of the paper electrodes usually reduce internal strain inside the electrodes during the long-term electrochemical cycling.^[16,42] It is worth noting that the flexibility of the here investigated electrodes is expected to be better than previous studies in which Young's modulus values were not clearly stated.^[35,39]

Figure 1c shows a SEM cross-section image of the MoO_{3-x} -CNTs-CC paper, which had a thickness of about 12 μm . Using a high magnification (Fig. 1d), it can be seen that the nanostructured MoO_{3-x} was uniformly distributed inside a matrix of randomly oriented CNTs-CC fibers. Likewise, the SEM top-view showed that the MoO_{3-x} is homogenously immobilized on the CNTs-CC matrix. The EDX mapping also confirmed that the MoO_{3-x} were embedded inside the CNTs-CC matrix (see Fig. S1). It should be mentioned that it is challenging to distinguish between the CNT and CC fibers since they have very similar diameters.^[24]

Figure 1: Synthesis and morphology of the MoO_{3-x} -CNTs-CC paper electrode: (a) schematic illustration of the paper electrode manufacturing process (b) photos of the paper electrodes showing their flexibility, (c) and (d) low and high magnification SEM cross-section images, respectively, showing the thickness and homogeneity of the electrodes. (e) SEM top-view image, displaying the uniform distribution of MoO_{3-x} on the CNTs-CC matrix.

To study the electrochemical properties of the MoO_{3-x} -CNTs-CC paper, cyclic voltammetric (CV) experiments were carried out between 0 and 0.50 V vs. Ag/AgCl (1 M KCl) in an electrolyte composed of 1.0 M H_2SO_4 . The open circuit potential (OCP) of the electrodes was about 0.25 V, and during the CV measurement the potential was swept from OCP down to 0 V, after which the scan was reversed to 0.5 V, i.e. the electrodes were first reduced and then oxidized. As seen in Fig 2a, the CVs obtained at a scan rate of 10 mV s^{-1} displayed two well-defined redox peaks, which can be assigned to the redox reactions of $\text{Mo}^{6+} \leftrightarrow \text{Mo}^{5+}$ and $\text{Mo}^{5+} \leftrightarrow \text{Mo}^{4+}$.^[43,44] The redox peaks located at about 0.19 V (cathodic peak) and 0.21 V (anodic peak) thus stem from the $\text{Mo}^{5+}/\text{Mo}^{4+}$ redox system while the peaks observed at about 0.29 V (cathodic peak) and 0.31 V (anodic peak) can be ascribed to the reduction of Mo^{6+} and oxidation of Mo^{5+} , respectively. As can be seen in Fig. 1a, the oxidation state of the molybdenum was

mainly +5 in the as-prepared MoO_{3-x}-CNTs-CC paper electrode (because the OCP was 0.25 V which is beyond the first reduction reaction of Mo⁶⁺ ↔ Mo⁵⁺ occurring at potential of 0.29 V, and thus Mo⁵⁺ is the dominant oxidation state at the OCP). Interestingly, the shapes of the voltammograms did not change during the first few cycles, as can be seen in Fig. 2a where the 1st (black), 2nd (red) and 11th (blue) cycles almost superimpose. This indicates that the electrochemical behavior of the MoO_{3-x}-based electrode was highly reversible. It worth noting that previous reports have shown that the CNTs also are electrochemically active and thus contribute to the measured capacity.^[24] In this study, the obtained capacity was therefore normalized using the mass of both the MoO_{3-x} and CNTs which correspond to about 90% of the electrode mass.

The shapes of the voltammograms in Fig. 2b also maintained their symmetries upon increasing the scan rate from 10 to 20, 50, and 100 mV s⁻¹, indicating that the kinetics of the electrochemical reactions was fast (with a scan rate of 100 mV s⁻¹ the durations of the oxidation and reduction scans were merely five seconds). Moreover, the average capacity, of about 30 C g⁻¹, was almost independent of the scan rate while the coulombic efficiency was close to 100% (see Fig. 2c and Fig. S2). In addition, the long-term cycling at high (1000 mV s⁻¹), moderate (50 mV s⁻¹), and low (10 mV s⁻¹) cycling rates showed a stable electrochemical behavior over about 10 000 cycles (see Fig. S2). This high rate performance reflects the fast kinetics of the redox reactions mentioned above. The contribution of the CNTs to the measured capacity was evaluated by testing CNTs-CC electrodes with a weight ratio of 1:1 and the discharge profiles showed that the CNT capacities were about 22 and 16 C g⁻¹ using current densities of 1 and 70 A g⁻¹, respectively (see Fig. S2d and e). Providing that the CNTs content in the MoO_{3-x}-CNTs-CC electrodes was about 20%, the CNTs would hence give rise to a contribution of about 3.3 to 4.5 C g⁻¹, i.e. 11 to 15% of the measured capacity (see Table S1).

It is worth noting that the specific capacity of the electrodes was quite low (i.e. 30 C g⁻¹), even though the capacity would increase slightly to about 40 C g⁻¹ upon normalization with respect to the MoO_{3-x} mass only (70% of overall electrode mass). However, the capacity is still much lower than the theoretical capacity of about 1339 C g⁻¹, i.e. the electroactive fraction of MoO_{3-x} is about 3%. This finding indicates that only the surface of the MoO_{3-x} layer immobilized on the CNTs-CC matrix was

electroactive.^[28] This hypothesis is also supported by the well-defined peak shape in CVs seen at the different scan rates, which indicates that the redox reactions were surface confined and not diffusion controlled. Figure 2g shows a schematic illustration of the MoO_{3-x} immobilized onto the CNTs-CC fiber, where it is assumed that only the surface MoO_{3-x} layer was electroactive. As this and the low mass loading (0.19 mg) resulted in a capacity of the electrodes of about 5.6·10⁻³ C, it is clear that the capacities of the present type of electrode, as well as many other electrodes described in the literature, are not well optimized for being used directly in high-capacity devices. Therefore, further research studies should be focused on developing electrodes with significantly higher mass loadings in which all the electroactive material can be readily accessed. One possible solution to increase the capacity of the MoO_{3-x}-CNTs-CC paper electrode could be to increase the lateral size of the MoO_{3-x} flakes as previously shown by Coleman et al.^[34]

The reversibility of the system was estimated from the variation of the peak-to-peak separation (ΔU_p) between the reduction and oxidation peaks (i.e., between peak 1 and 1', and between peak 2 and 2', respectively) as a function of the scan rate.^[28,44] As seen in Fig. 2 d, ΔU_p remained lower than 50 mV at the different scan rates. The linear increase in the peak-to-peak separation upon increasing the scan rate from 10 to 100 mV s⁻¹ can mainly be attributed to iR (i.e. ohmic-drop) effects.^[4,45] This observation is further supported by the fact that the peak-to-peak separations between peak 1 and 2, and between peak 1' and 2', respectively were independent of the scan rate (inset in Fig. 2d). A plot of the *logarithm* of the absolute value of the peak current as a function of the *logarithm* of the scan rate (Fig. 2e and f) indicates that the redox reaction was surface confined as the obtained slopes were very close to unity (0.89 - 0.97). This behavior further supports the aforementioned hypothesis regarding the electroactivity of only the surface of the oxide layer deposited within the CNTs-CC matrix.

Figure 2: Studying the electrochemical performance of the MoO_{3-x}-CNTs-CC paper electrodes using cyclic voltammetry: (a) and (b) voltammograms recorded at a scan rate of 10 mV s⁻¹ and different scan rates, respectively. The arrows in (a) indicate the scan direction. (c) The capacity and coulombic efficiency as a function of the scan rate. (d) The peak-to-peak separations (ΔU_p) as a function of the scan rate for redox peaks 1 and 1' (black), and redox peaks 2 and 2' (red). The inset displays the dependence of ΔU_p on the scan rate for the reduction-reduction (black) peaks and the oxidation-oxidation (red) peaks. (e) and (f) The *logarithm* of the peak current (i_p) as a function of the *logarithm* of the scan rate for peaks 1 and 1', and peaks 2 and 2', respectively. (g) Schematic illustration of the MoO_{3-x} immobilized onto CNTs-CC fiber showing the thin electroactive layer of MoO_{3-x}.

Constant current charge and discharge curves were also recorded for the MoO_{3-x} -CNTs-CC paper electrodes. As can be seen in Fig. 3a, the observed behavior was analogous to that seen in the CV experiments. Both the discharge (i.e. reduction) and charge (i.e. oxidation) curves thus featured two plateaus at about 0.29 and 0.19 V and 0.30 and 0.20 V, respectively, for an applied current density of 0.78 A g^{-1} . In Fig 3c, superimposed discharge profiles can be seen for current densities of 0.78 and 7.8 A g^{-1} in good agreement with the high rate performance and iR drop discussed above. Furthermore, the capacity remained almost constant and the coulombic efficiency stayed close to 100% when increasing the current density up to 78 A g^{-1} as shown in Fig. 3e and S3. It worth mentioning that, the applied currents were 100 μA and 10 mA at current densities of 0.78 and 78 A g^{-1} , respectively due to the relative low amount of electroactive material. These low currents explain why the increase in the iR drop was relatively quite low when increasing the applied current density by an order of magnitude. The small increase in the iR drop combined with the fact that the redox reactions are surface confined explain why the accessible capacities and the coulombic efficiency remained unchanged although the current density was increased by a factor of ten and the cut-off voltages remained the same (0 and 0.5 V for the lower and upper cut-off limits, respectively). These results hence clearly indicate that the magnitude of the iR drop and hence also the dependence of the capacity of the cycling rate is strongly dependent on the electroactive mass of the electrodes. For example, the discharge profiles for electrodes with larger sizes (5 mm x 7 mm) and mass loadings (total mass 320 μg) showed more pronounced iR drops and a decrease in the electrode capacity (see Fig. S3c) especially at high current density of 70 mA g^{-1} (corresponding to about 20 mA absolute current). Care should therefore be taken when comparing rate performances of different electrodes particularly as quite low mass loadings often are used in many studies even though their capacities are too low to be of practical importance. As the current used in constant current experiment depends linearly on the mass loading of the electroactive components it is immediately evident that significantly larger iR drops and hence lower capacities will be seen when using electrodes with higher mass loadings unless the increased iR drop is compensated for by an appropriate adjustment of the cut-off limits.

The MoO_{3-x}-CNTs-CC paper electrodes were also cycled for about 11 000 cycles with a current density 7.8 A g⁻¹. The capacity retention was about 91%, and the coulombic efficiency was about 100% which indicates a high reversibility of the redox reaction and the absence of parasitic reactions (see Fig. 3b). The observed small capacity loss can be attributed to the dissolution of the MoO_{3-x} in the electrolyte.^[30,46,47] As seen in Fig 3d and f, the capacity retentions were about 95 and 97 %, respectively, when the MoO_{3-x}-CNTs-CC electrode was further cycled for 8000 and 14 000 cycles at current densities of 39 and 78 Ag⁻¹, respectively. These results indicate that the MoO_{3-x}-CNTs-CC paper electrode can be cycled over 30 000 cycles without a major capacity loss (see Fig S4). In addition, the morphology of the MoO_{3-x}-CNTs-CC electrode remained almost unchanged after long-term cycling (see Fig. S4c).

It was shown previously that the accessible capacity of the MoO_{3-x} nanosheets drop significantly as the loading of the electrodes increased from 6.25 to 50 µg cm⁻².^[28] For instance, when the loading was about 50 µg/cm² (corresponding to thickness about 8-11 µm) the capacity dropped to about 20 and 10 C g⁻¹ at scan rates of 20 and 1000 mV/s, respectively. In the present study, we successfully increased the mass loading to about 0.9 mg cm⁻² (corresponding to thickness about 12 µm) and achieved a capacity of about 30 C g⁻¹ at scan rates of 20 or 1000 mV/s. Furthermore, the long-term cycling was previously limited to about 2000 cycles,^[28] however, in this study we achieved a cycling stability over 30 000 cycles. These observations clearly approve that the immobilization of nanostructured MoO_{3-x} onto 3D network of CNTs-CC fibers can successfully improve the accessible capacity, rate capability, and long-term cycling. Therefore, the accessible capacity of the MoO_{3-x}-CNTs-CC electrodes is not so promising compared to theoretical one, however, it is superior compared to a previous study on same material.^[28] Table S2 includes a comparison of the performances of the present MoO_{3-x}-CNTs-CC electrodes as well as those of other MoO₃ based electrodes reported in the literature. While it can be seen that this MoO_{3-x}-CNTs-CC electrode did not show a superior gravimetric capacity; ^[11,28,35,38] an excellent high rate performance and long-term cycling stability was found for electrodes with a mass loading about 0.9 mg cm⁻².

All in all, the excellent electrochemical stability and high rate performance can be attributed to the high reversibility of the redox surface confined reactions, homogenous distribution of the oxide layer

over the conductive nanofibril network, the absence of diffusion limitations, small increase in the iR drop upon increasing the current density due to the low applied current (resulting from the relatively low mass loading), and the accommodated internal strain inside the flexible paper electrodes.^[16,42] The specific gravimetric capacity can be improved by using 3 M H_2SO_4 solution, probably due to lower iR drop and higher ionic conductivity (see Fig. S5). However, the capacity fading is highly pronounced, most likely due to dissolution of the oxide and degradation of the CNTs–CC network by the strong oxidizing acidic electrolyte.^[30,46,47] Further electrochemical and analytical studies are still needed to understand the electrochemical behavior of the MoO_{3-x} –CNTs–CC electrodes in 3 M H_2SO_4 .

Figure 3: The electrochemical behavior of MoO_{3-x}-CNTs-CC paper electrodes under constant current conditions: (a) Charge and discharge curves for at current density of 0.78 A g⁻¹. (c) Discharge profiles for current densities of 0.78 and 7.8 A g⁻¹, respectively. (e) The capacity and coulombic efficiency as a function of the current density. (b), (d) and (f) The discharge capacity (red), capacity retention (black), and coulombic efficiency (blue) as a function of the cycle number, for current densities of 7.8, 39, 78 A g⁻¹, respectively.

3. Conclusions:

In summary, flexible MoO_{3-x} -CNTs-CC paper electrodes were prepared using a straightforward and robust filtration-based method. SEM combined with EDX showed that the electrode thickness was about 12 μm and the molybdenum oxide was uniformly distributed within the CNTs-CC matrix. The MoO_{3-x} -CNTs-CC delivered a reversible capacity of 30 C g^{-1} at current densities between 0.78 and 78 A g^{-1} . The comparatively low capacity value suggested that only the surface layer of the oxide was electroactive. The long-term cycling of the electrodes shows that the electrodes can be cycled for more than 30 000 cycles without a major capacity loss or a drastic structural change in the active material.

The analysis of the peak currents and potentials for the redox peaks seen in the CVs showed that the electrode kinetics were fast, and that the polarization was mainly due to the iR drop. The outstanding cyclability and rate capability of the MoO_{3-x} -CNTs-CC electrodes can be mainly attributed to four factors: (1) the nature of the redox reaction is surface confined, (2) absence of diffusion limitations, (3) high electronic conductivity and flexibility of the electrodes, and (4) the increase in iR drop with the current density is quite low due to the relative low mass loading and lateral dimensions of the electrodes used in the electrochemical experiments.

4. Experimental:

4.1. Preparation of the paper electrodes:

The flexible free-standing electrodes were prepared according to the previously reported protocol^[23,24], with some modification as explained below. In a typical experiment, 70 mg of MoO_{3-x} nanosheet powder (prepared as previously described),^[28] 20 mg multi-walled CNTs, and 10 mg of *Cladophora* cellulose were added to a mixture containing 60 mL water and 20 mL ethanol. The obtained mixture was subjected to sonication for 20 min using a high energy ultrasonic equipment (Sonics and Materials Inc., USA, Vibra-Cell 750) under water cooling. The mixture was then drained on a polypropylene filter to form a filter cake and subsequently dried to form a paper sheet. The paper sheet could be directly used as a freestanding electrode with an active mass (mass of MoO_{3-x} and CNTs) loading of 0.9 mg cm^{-2} , and the overall electrode weight including the nanocellulose was about 1 mg cm^{-2} .

². Likewise, the CNT-CC paper electrode were prepared using a mixture of CNT and CC of 1:1 weight ratio.

4.2. Material characterization and electrochemical measurements:

The morphology and elemental mapping of the electrodes were explored using a Scanning Electron Microscope (SEM, LEO 1550 Gemini) equipped with an energy-dispersive X-ray (EDX) detector. X-ray diffraction (XRD) measurements were performed using a PANalytical diffractometer, equipped with Cu K α radiation ($\lambda = 1.54\text{\AA}$). The Young Modulus for the MoO $_{3-x}$ -CNTs-CC paper was obtained from nanoindentation tests using a Hysitron Ti950 tribointegrator device equipped with a Berkovich indenter. An array of 3x3 indentations with a trapezoidal loading profile was used together with a 1000 μN peak load. A standard fused silica was used for calibrating the instrument prior the measurements. The electronic conductivity of the MoO $_{3-x}$ -CNTs-CC paper was determined using a Jandel Four Point Probe system (with a 0.63 mm probe spacing).

All electrochemical measurements were performed in a three-electrode configuration using a stainless-steel Swagelok cell with activated carbon (YP-50, Kuraray, Japan) as the counter electrode and an Ag/AgCl (1 M KCl) reference electrodes. The MoO $_{3-x}$ -CNTs-CC electrodes used as the working electrode were placed on a gold foil current collector. A piece of *Celgard* 3501 soaked in 1 M H $_2$ SO $_4$ was used as the separator. The overall working electrode mass varied between 100 and 210 μg and the capacities were normalized with respect to the mass of the redox-active materials, i.e. the MoO $_{3-x}$ and carbon nanotubes (CNTs). The electrodes lateral dimensions were about 2-3 mm. Few experiments were performed using electrodes of dimension (5mm x 7mm) and mass loading of 320 μg . Cyclic voltammetry and constant current techniques were used to study the electrochemical behavior of the electrodes in the potential window between 0 and 0.50 V vs. Ag/AgCl (1 M KCl). For the experiments done using CNTs-CC electrodes, the overall working electrode mass was about 180 μg (2-3 mm lateral dimensions) and the capacities were normalized with respect to the mass of CNTs, i.e. 50% of total electrode mass.

Supporting Information:

XRD data, EDX mappings, cyclic voltammograms and constant current charge and discharge curves are available in the supporting information.

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