

Article Ammonium Ion-Pre-Intercalated MnO₂ on Carbon Cloth for High-Energy Density Asymmetric Supercapacitors

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Abstract: With the continuous development of green energy, society is increasingly demanding advanced energy storage devices. Manganese-based asymmetric supercapacitors (ASCs) can deliver high energy density while possessing high power density. However, the structural instability hampers the wider application of manganese dioxide in ASCs. A novel MnO₂-based electrode material was designed in this study. We synthesized a MnO₂/carbon cloth electrode, CC@NMO, with NH₄⁺ ion pre-intercalation through a one-step hydrothermal method. The pre-intercalation of NH₄⁺ stabilizes the MnO₂ interlayer structure, expanding the electrode stable working potential window to 0–1.1 V and achieving a remarkable mass specific capacitance of 181.4 F g⁻¹. Furthermore, the ASC device fabricated using the CC@NMO electrode and activated carbon electrode exhibits excellent electrochemical properties. The CC@NMO //AC achieves a high energy density of 63.49 Wh kg⁻¹ and a power density of 949.8 W kg⁻¹. Even after cycling 10,000 times at 10 A g⁻¹, the device retains 81.2% of its capacitance. This work sheds new light on manganese dioxide-based asymmetric supercapacitors and represents a significant contribution for future research on them.

Keywords: manganese dioxide; ammonium ions; pre-intercalation; carbon cloth; asymmetric supercapacitor; high energy density

1. Introduction

Energy storage technology holds a crucial position in the technological transformation of modern society. With the speedy growth of renewable energy and electrification technologies, there is a rising demand for novel devices with high efficiency, quick response times, and reliability [1–3]. In this context, supercapacitors (SCs) have garnered widespread attention as highly promising energy storage device. SCs offer a fast charge/discharge capability, extended service life, and great power density [4–6]. However, conventional supercapacitors still face limitations in terms of energy density. To address this challenge, the concept of asymmetric supercapacitors (ASCs) has emerged [7,8]. ASCs combine the characteristics of electrochemical and double-layer capacitors, aiming to deliver higher energy density, along with high power density. The two electrodes in ASCs are typically divided into battery-type and capacitor-type electrodes. Enhancing the electrochemical behavior of battery-type electrodes is the primary focus of ASC research due to its significant contribution to the high energy density of ASCs [9–11].

Among the substrate materials for ASC electrodes, carbon cloth (CC) is a non-metallic substrate with a large specific surface area and outstanding mechanical properties. In contrast to metallic substrates, CC can be stabilized in acidic and alkaline electrolytes [12]. However, carbon cloth has a series of disadvantages, such as its hydrophobicity and poor adhesion of active substances. Therefore, the CC needs to be pretreated to improve its adhesive performance. Pretreated CC is an ideal substrate material for ASC electrodes and can easily load pseudo-capacitance materials using synthesis methods such as the hydrothermal method [13].



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Metal oxides are widely used as ASC electrode materials. Among the various metal oxides, manganese dioxide is an electrode material deserving of attention because of its excellent energy storage performance and low cost. Its high specific surface area and abundant controllable redox reactions have garnered a lot of focus in research on ASC devices [14]. However, MnO₂ has defects such as its poor electronic conductivity and unstable structure, which hinder its further development. Improving the microstructure has been the focus of MnO₂-based electrode research. There is a variety crystal structures of MnO₂, such as α , β , γ , δ , etc. Unlike the chain/tunneling-type structures possessed by α , β , and γ -MnO₂, the layered structure of δ -MnO₂ provides more possibilities for improving the electrochemical performance of MnO₂ [15].

Pre-intercalation technology has received much attention as a strategy that can significantly enhance the electrochemical behavior of materials [16]. By pre-intercalating ions into the layered structure, it is possible to stabilize the crystal structure, optimize its electronic conduction properties, and improve responsiveness to electrons. The pre-intercalation technique that has been reported so far mainly involves Na⁺, K⁺, Cu²⁺, Zn²⁺, Al³⁺, and Sn⁴⁺ [17–24]. Compared with these ions, NH₄⁺ has a lower molar mass, which can improve the mass specific capacity of MnO₂ materials. NH₄⁺-pre-intercalated vanadium oxides have been used in energy storage applications, and the NH₄⁺ ions contribute to facilitating the fast kinetics of ions/electrons and enhancing structural stability [25]. However, no studies about ammonium ion-pre-intercalated manganese oxides for ASCs have been reported.

In this study, we synthesized a manganese dioxide/carbon cloth electrode with ammonium ion pre-intercalation (CC@NMO) using a one-step hydrothermal method, as shown in Figure 1. Via NH₄⁺ pre-intercalation, the potential window of CC@NMO can be widened from 0–0.8 V to 0–1.1 V against the pure MnO₂/carbon cloth (CC@MnO₂) electrode. The CC@NMO electrode was found to have a remarkable capacitance of 181.4 F g⁻¹. After being matched with the activated carbon electrode, the CC@NMO electrode was fabricated into a lithium-ion asymmetric supercapacitor (CC@NMO//AC). The energy density of CC@NMO//AC can reach 63.49 Wh kg⁻¹, with a power density of 949.8 W kg⁻¹. Furthermore, under a high current density of 20 A g⁻¹, the energy density can be kept at 31 Wh kg⁻¹. After complete cycling for 10,000 cycles at 10 A g⁻¹, there is still 81.2% capacitance retention. This work explores the effective improvement of the capacitance properties of MnO₂ through NH₄⁺ ion pre-intercalation technology, presenting a new future for high-energy density ASCs.



Figure 1. Schematic diagram of the synthesis of CC@NMO.

2. Materials and Methods

2.1. Pretreatment of CC

The carbon cloth (CC) was cut into 3 cm \times 4 cm rectangles and cleaned using deionized water (DIW). The cleaned rectangular CC was ultrasonicated in an acetone solution for 10 min, then ultrasonicated with ethanol for another 10 min; this procedure was repeated three times. Finally, the pretreated CC was put into an oven for drying overnight at 60 °C. Due to the pretreatment and activation of CC, more active sites appeared around the surface of the carbon fibers, enhancing its adhesion to the MnO₂ [17].

2.2. Synthesis of CC@NMO

KMnO₄ (0.237 g, 1.5 mmol) and CH₃COONH₄ (0.038 g, 0.5 mmol) were dissolved in 30 mL DIW and stirred until completely mixed. Then, the pretreated CC was transferred to a 50 mL solution with a Teflon-lined autoclave. The hydrothermal reaction was carried out at 120 °C, lasting for 3 h. After being rinsed with DIW and ethanol, the CC@NMO electrode was cut into 1 cm \times 1 cm. The mass loading of the CC@NMO electrode should be 1 mg on a slice of CC with an area of 1 cm².

2.3. Fabrication of CC@NMO//AC ASC Device

To fabricate an ASC device, CC@NMO is used as a cathode, with activated carbon (AC) serving as an anode. Depending on charge conservation, there is a need for an exact match between cathode and anode. The mass ratio of both electrodes is estimated using the following:

$$\frac{\mathbf{m}_{+}}{\mathbf{m}_{-}} = \frac{\mathbf{C}_{-} \cdot \Delta \mathbf{V}_{-}}{\mathbf{C}_{+} \cdot \Delta \mathbf{V}_{+}} \tag{1}$$

in which C represents the mass specific capacitance (F g⁻¹); ΔV stands for the stably working potential window (V). The mass loading of the AC electrode should be 2 mg, according to Equation (1). After matching the electrodes, an ASC device was fabricated with the two electrodes and 1 M Li₂SO₄ solution as the electrolyte.

The AC electrode was prepared as follows: active carbon (AC), Super P, and polyvinylidene fluoride (PVDF) binder in a weight ratio of 7:2:1 were dispersed in N-methylpyrrolidone (NMP) solvent. According to the electrode match, the loading mass of AC should be 2 mg. After stirring, the homogeneous slurry was coated uniformly on a copper foil. After vacuum-drying, it was cut into discs to be used as the electrodes. Then, CR2032-type coin cells were assembled with the two electrodes, glass fiber as a separator, and 1 M Li₂SO₄ solution as the electrolyte. After all the processes above, the two-electrode ASC device was finally fabricated.

2.4. Characterization

Scanning electron microscopy (SEM) images were obtained using a Zeiss sigma-300 thermal field emission scanning electron (Zeiss, Oberkochen, Germany) microscope to characterize the surface micromorphology of the samples. The existence of elements in the material was characterized using an energy dispersion spectrometer (EDS). To characterize the crystal structures of the samples, their X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance (Bruker, Bremen, Germany) using Cu K α radiation ($\lambda = 0.15406$ nm) with 20 degree ranging from 10° to 80°. Fourier-Transform Infrared Spectroscopy (FTIR, Thermo Fisher, Waltham, MA, USA) was used to reflect the chemical constitution and crystalline structure, with the wavenumber ranging from 4000 to 400 cm⁻¹. X-ray photoelectron spectroscopy (XPS, Axis Supra, and Kratos, Manchester, UK) was conducted to further verify the elements' existence and evaluate their valence states.

2.5. Electrochemical Measurements

To evaluate the electric behavior of the CC@NMO, we assembled a three-electrode system for electrochemical testing utilizing a saturated calomel electrode, along with a platinum electrode. Cyclic voltammetry (CV) experiments and galvanostatic charge/discharge (GCD) experiments were carried out by using a CHI660e workstation with 1 M Li_2SO_4 as the electrolyte. The capacitance of the CC@NMO electrode can be determined through the GCD curves using the following equation:

$$C = \frac{I \cdot \Delta t}{m \cdot \Delta V} (F \cdot g^{-1})$$
⁽²⁾

in which I denotes the current density (A), Δt represents the time used for discharging (s), m denotes the material weight, and ΔV stands for the voltage window for the GCD test (V).

To further demonstrate the contribution to the high capacity and energy density of CC@NMO, an ASC device was fabricated using CC@NMO as the cathode and AC as the anode. The CV experiments and GCD experiments were also carried out by using a CHI660e electrochemical workstation. The mass specific capacitance of ASC could be obtained from the GCD curve based on Equation (2). The formulas for calculating the energy density and power density of ASC are as follows:

$$E = \frac{1}{2} \cdot \frac{1}{3.6} C \cdot V^2 \; (Wh \cdot kg^{-1}) \tag{3}$$

$$P = \frac{E}{t} \cdot 3600 \; (W \cdot kg^{-1}) \tag{4}$$

where C denotes the mass specific capacitance of ASC (F g^{-1}), V represents the voltage range of ASC (V), and t is the time used for discharging (s) [7].

3. Results

The SEM images are displayed in Figure 2, revealing the morphology of CC@NMO. From Figure 2a, it can be seen that after ultrasonic treatment in acetone, the surface of the carbon cloth is visible. The wrinkles on the carbon fibers provide active sites for the adhesion of MnO₂. Figure 2b shows the morphology of CC@MnO₂, and it can be seen that there are layered MnO_2 nanosheets on the carbon cloth fibers. Additionally, there are some MnO_2 nanoflowers, which are assembled from the MnO_2 nanosheets. The carbon cloth and MnO_4^- ions react as follows: $4MnO_4^- + 3C + 4H^+ \rightarrow 4MnO_2 + 2H_2O + 3CO_2\uparrow$. This promotes the transition from KMnO₄ to MnO₂ [26]. Figure 2c displays the SEM image of CC@NMO. After NH₄⁺ pre-intercalation, the CC@NMO can retain the morphology without structural collapse. The NMO nanoflowers are clearly recognizable, as are the layered nanosheets. An image of the MnO₂-covered part and the uncovered part in CC@NMO is displayed in Figure 2d. It is evident that a δ -MnO₂ layer with a complex laminar structure has been loaded. Figure 2e-g show the results of our EDS elemental mapping analysis of this region, corresponding to the elements C, O, and Mn. It can be inferred that MnO_2 nanoflowers form a coating structure around the surface of the CC. Figure 2h presents the high magnification of MnO_2 nanoflowers with a diameter of 500 nm. The nanoflowers are assembled from two-dimensional (2D) ultra-thin nanosheets. This unique structure provides abundant active sites for energy storage, which help the CC@NMO sample to obtain a larger specific capacitance [27]. Through EDS elemental mapping analysis, as shown in Figure 2i-k, the nitrogen element is uniformly distributed around the NMO nanoflowers. TEM and HRTEM images are shown in Figure S1. Figure S1a indicates that the NMO nanoflowers are assembled from layered 2D nanosheets. Moreover, from the HRTEM image (Figure S1b), the distinct lattice fringes of 0.7 nm are assigned to the (001) lattice planes of NMO. All of the above evidence that the NH4⁺ ions are successfully intercalated into NMO, with no structure being destroyed.

X-ray diffraction (XRD) can characterize the phase concentration and crystal structure. The XRD spectra of CC@MnO₂, CC@NMO, and CC are shown in Figure 3a. Compared with CC, there are obvious diffraction peaks of CC@MnO₂ and CC@NMO. The obvious peaks located around 12.5°, 25°, 37.1°, and 65.5° precisely satisfy the peaks of δ -MnO₂ (JCPDS: 80-1098), which represent (001), (002), (-111), and (020) crystal planes, respectively [27]. The

four main characteristic peaks, as well as the absence of other impurity peaks, indicate the successful synthesis of MnO_2 loaded onto CC. Notably, the (001) peak of the CC@NMO sample has a smaller degree than that of the CC@MnO₂ sample, as shown in Figure S2. According to Bragg's Law, the CC@NMO obviously has larger interplanar spacing. This phenomenon is consistent with that of MnO_2 electrodes pre-intercalated with other ions. The (001) plane of MnO_2 is our main research subject. Due to the intercalation of NH_4^+ , the layer spacing of CC@NMO has been expanded. All of these make the CC@NMO capable of providing a larger space for accelerating ion/electron kinetics [28].



Figure 2. Morphological analyses: (**a**) pretreated CC; (**b**) CC@MnO₂; (**c**) CC@NMO; (**d**) low magnification of CC@NMO; (**e**–**g**) EDS mapping of C, O, and Mn; (**h**) high magnification of CC@NMO; and (**i–k**) EDS mapping of N, O, and Mn.

Fourier-Transform Infrared Spectroscopy (FTIR) was used to further investigate how NH₄⁺ intercalates into MnO₂. Figure 3b displays the FTIR spectra of CC@NMO and CC@MnO₂. The lattice vibration of Mn-O can be seen between 400 cm⁻¹ and 500 cm⁻¹, indicating the successful loading of MnO₂ [29]. The peaks appearing near 1670 cm⁻¹ and 3400 cm⁻¹ correspond to O-H bending/stretching vibration modes. This phenomenon proves the existence of constitution water molecules between the MnO₂ layers. Interestingly, it has been proven that the water molecules between the layers can reduce the effect of positive ion electrostatic repulsion, thus promoting the positive ion migration rate [30]. The existence of hydrogen bonding can also increase the charge density of the electrode material [31]. From the spectrum, we can observe that compared with CC@MnO₂, there is a characteristic peak at 1409 cm^{-1} for CC@NMO, which belongs to the N-H bending mode. The peak around 3200 cm^{-1} , corresponding to the hydrogen bonding of N-H, indicates the characteristic N-H \cdots O stretching vibration [32]. All the above demonstrates how NH₄⁺ ions and water molecules exist in the interlayers of the CC@NMO samples. As interlayer structural columns, NH4⁺ ions improve the structural stability of MnO₂. They can allow the interlayer spacing to expand, accelerating the transport of the ions. Additionally, the water molecules also increase the electrochemical rate of the CC@NMO electrode. Overall, the unique interlayer structure provides strong support for raising the energy density of ASCs [33].

(a)

Intensity (a.u.)

10

(c)

Intensity (a.u.)

0

(e)

Intensity (a.u.)





Figure 3. (a) XRD patterns of CC@NMO, CC@MnO₂, and CC; (b) FTIR spectra of CC@NMO and CC@MnO₂; and (c) XPS spectra of CC@NMO, (d) Mn 2p, (e) O 1s, and (f) N 1s.

The elemental components and chemistry information of a sample can be provided through X-ray photoelectron spectroscopy (XPS). Figure 3c shows the survey spectrum of CC@NMO, with C, O, Mn, and N elements clearly existing. From the spectrum of Mn2p (Figure 3d), the peaks located at 642 and 653.7 eV can be clearly seen. They are assigned

to Mn $2p^{3/2}$ and Mn $2p^{1/2}$, respectively [34]. The two peaks are separated by a difference of 11.7 eV, satisfying the characteristic of Mn⁴⁺ in MnO₂. Figure 3e is the O 1s spectrum, and the 529.2 eV, 530.4 eV, and 533.0 eV characteristic peaks correspond to Mn-O-Mn, Mn-O-H, and H-O-H bonds, respectively [35,36]. Figure 3f shows the spectra of N 1 s, and the binding energy characteristic peak at 399.6 eV further proves the N element exists. Through all of the above, the existence of NH₄⁺ ions can be clearly verified, and they are successfully pre-intercalated into the interlayer of MnO₂ [33].

To test the electrochemical behavior of the CC@NMO, it is necessary to confirm the electrode's stable working potential window by cyclic voltammetry (CV) testing [37]. Figure 4a depicts the CV curves of CC@MnO₂ at a range of potential windows under 5 mV s^{-1} . The CV shape of CC@MnO₂ remains approximately rectangular at 0–0.8 V. The peak polarization is more obvious when the potential window exceeds 0.9 V, indicating that the CC@MnO₂ electrode only works stably in the range of 0–0.8 V [38]. The stable working potential window of the pure MnO₂ electrode under the neutral aqueous electrolyte is consistent with previous studies [39,40]. In contrast, the CV curves of CC@NMO are at enlarged potential windows at 5 mV s^{-1} (as shown in Figure 4b), which keeps approximately rectangular until it exceeds 1.1 V. After NH₄⁺ pre-intercalation, the stable working potential window of the CC@NMO electrode was significantly escalated to 0–1.1 V. Interestingly, this phenomenon is consistent with that of other ion-pre-intercalated MnO₂ electrodes [41]. Due to the structural support provided by NH₄⁺, the structural stability of NMO has been greatly enhanced [25]. Therefore, the CC@NMO electrode can maintain stability at a larger potential window, which makes it possible to fabricate a higher-energy density ASC.

Figure 4c shows a comparison of the CV behavior of both samples at 1 mV s⁻¹. Notably, CC@NMO has redox peaks at 0.15 V and 0.75 V, whereas the CC@MnO₂ electrode exhibits approximately rectangular peaks. The CC@NMO's pseudo-capacitance behavior provides a more adequate chemical reaction at the electrode, leading to a larger CV curve area and enhancing the specific capacitance [42]. As depicted in Figure 4d, the shapes of the CV curves are approximately ideal rectangles at different scan rates. Even at a high scan rate, the CC@NMO electrode still maintains a fast ion diffusion rate and exhibits great capacitance performance. The EIS curves of CC@MnO₂ and CC@NMO in a three-electrode system are shown in Figure S3. For the two electrodes, the EIS curves represent a minor semicircle in the high-frequency section and an almost vertical diagonal line in the low-frequency section. The equivalent series resistance value of 2.54 Ω of the CC@NMO electrode is much lower than CC@MnO₂ (3.51 Ω). Additionally, the slope of the CC@NMO electrode in the low-frequency section is steeper than that of the CC@NMO electrode. The EIS curves reveal that CC@NMO has faster charge transfer and ion diffusion because of NH₄⁺ pre-intercalation.

The GCD curves of the CC@NMO electrode (shown in Figure 4e) reflect the capacity performance. The charging and discharging time can be as long as 390 s at 1 A g^{-1} , which indicates that CC@NMO has excellent capacitive behavior. Moreover, the triangle-like GCD curves can maintain their shape with the gradual increase in current density. Meanwhile, the stable triangular GCD curves mean the electrode has excellent charge/discharge stability and good reversibility [28,43]. The GCD curves of CC@MnO2 in three-electrode systems are shown in Figure S4. The mass specific capacitance can be calculated by Equation (2). As displayed in Figure 4f, at 1 A g^{-1} , the capacitance of CC@NMO is as high as 170.17 F g^{-1} . The capacitance of the CC@NMO electrode can still remain at 109.09 F g^{-1} at 20 A g^{-1} . At a current density of 0.5 A g⁻¹, the capacitance of CC@MnO₂ is 126.7 F g^{-1} , which is much lower than the capacitance of CC@NMO (181.4 F g^{-1}). The cycling test of CC@NMO under a current density of 5 A g^{-1} in a three-electrode system is shown in Figure S5. For the first four cycles, the capacitance of CC@NMO is 147 F g^{-1} . After 500 cycles, the capacitance of CC@NMO can remain 145.65 F g^{-1} . The CC@NMO shows excellent cycle stability, with a very low capacitance loss. Obviously, the CC@NMO electrode has extraordinary capacitance performance and charging/discharging stability. In general, the CC@NMO electrode is an excellent choice for asymmetric supercapacitors.



Figure 4. (a) CV curves of CC@MnO₂ at different potential windows at 5 mV s⁻¹, (b) CV curves of CC@NMO at different potential windows at 5 mV s⁻¹, (c) comparison of CC@NMO and CC@MnO₂ at 1 mV s⁻¹, (d) CV curves of CC@NMO electrode at different scan rates, (e) GCD curves of CC@NMO electrode at different current densities, and (f) specific capacitance comparison of CC@NMO electrode and CC@MnO₂ electrode at different current densities.

For further examination of the capacitive behavior and contribution to the energy density of the CC@NMO electrode in ASCs, an aqueous ASC was fabricated. CC@NMO was used as the cathode, while activated carbon (AC) was used as the anode. Before the fabrication, the capacitance of the cathode and anode need to match exactly [17]. Figure 5a shows the CV results of AC in different potential windows at 5 mV s⁻¹. The AC electrode works stably from -0.1 to -1.1 V. Figure 5b shows a comparison between CC@NMO and AC at 5 mV s⁻¹. Figure S6a shows the GCD curves of the AC electrode at different current densities in -0.1 to -1.1 V. The specific capacitance of AC can be calculated from the GCD curves, as shown in Figure S6b. At 5 A g⁻¹, the specific capacitance of AC is 76.75 F g⁻¹, which is nearly half of the capacitance of CC@NMO. Obtained by Equation (1), the mass ratio of NMO and AC should be 1:2. The CC@NMO electrode and AC electrode were fabricated into an ASC device (CC@NMO//AC), with 1 M Li₂SO₄ as the electrolyte. The electrochemical behavior of CC@NMO//AC is plotted in Figure 6.



Figure 5. (a) CV curves of AC electrode at different potential windows at a 5 mV s⁻¹ scan rate; (b) CV curves of the cathode and anode at 5 mV s⁻¹.

Figure 6a shows the CV results of CC@NMO//AC at 5 mV s⁻¹. The shape of the curve still retains an ideal rectangular shape at 0-1.9 V, which reflects the electrical doublelayer capacitors (EDLCs)' property of having activated carbon electrodes. Meanwhile, the obvious redox peaks are consistent with the Faraday reaction of the NMO electrodes [44]. Figure 6b displays CV plots of CC@NMO//AC at rising scan rates. Excitingly, the CV shape still maintains its original form when the scan rate rises. The curves do not show significant deformation, and the redox peaks are still obvious at high scan rates, which indicates that the CC@NMO//AC has good capacitive performance and stability [28]. Figure 6c shows the EIS curve of CC@NMO//AC. In the high-frequency region, the shape of the EIS curve is semicircular, while the curve turns to a straight line with a 45° slope in the low-frequency region. The CC@NMO//AC has a small equivalent series resistance Rs, which is only 2.2 Ω . Figure 6d displays the GCD data of the CC@NMO//AC at different current densities. The charging and discharging time can reach up to 490 s at 1 A g^{-1} , showing excellent capacitance capacity. Due to the joint action of the EDLC and Faraday capacitor, the shape of the curve is a twisted triangle [17]. As the current density increases, the GCD curve still maintains the approximate triangle, which reveals the good capacitance characteristics and excellent charge/discharge stability of CCNMO//AC. According to Equation (2), the capacitance of CC@NMO//AC can be obtained from the GCD curve. As displayed in Figure 6e, at 1 A g^{-1} , the specific capacitance of ASC can reach 126.63 F g^{-1} and can be maintained at 61.8 F g^{-1} at 20 A g^{-1} . The relationship between the energy density and power density of CC@NMO//AC can be obtained from a Ragone plot, which can be calculated using Equations (3) and (4). As shown in Figure 6f, the energy density of CC@NMO//AC is up to 63.49 Wh kg⁻¹ at 1 A g⁻¹, while the power density is



949.8 W kg⁻¹. Interestingly, when the current density reaches 20 A g⁻¹, the energy density can still remain at 30 Wh kg⁻¹.

Figure 6. (a) CV curves of CC@NMO//AC at different voltage windows, (b) CV curves of CC@NMO//AC at different current densities, (c) EIS curve of CC@NMO//AC, (d) GCD curves of CC@NMO//AC at different current densities, (e) specific capacitance of CC@NMO//AC, and (f) Ragone plot of CC@NMO//AC.

Figure 7a shows a comparison between our CC@NMO//AC and other ASC devices mentioned in recently published research articles [45–54]. Obviously, our CC@NMO//AC

outperforms other Mn-based or CC-based devices in terms of energy density. Furthermore, the low cost and simple preparation process needed to synthesize our CC@NMO//AC make our work stand out compared to works about other MnO₂-based ASCs. Figure 7b displays the long cycling stability of our CC@NMO//AC. After completely cycling for 10,000 times at 10 A g⁻¹, the CC@NMO//AC still has 81.2% capacitance retention, which indicates that the device has excellent cycling stability. A comparison of capacitance retention between the CC@MnO₂//AC and CC@NMO//AC is shown in Figure S7. It can clearly be observed that after 10,000 cycles, the capacitance retention of the CC@MnO₂//AC decreases quickly, becoming only 74.2%. The structural enhancement of the pre-intercalated NH₄⁺ ions can significantly reduce the capacity reduction problem caused by structural instability during cycling [33].



Figure 7. (a) Ragone plots of CC@NMO//AC compared to recently reported results; (b) cycling stability of CC@NMO//AC at 10 A g^{-1} .

To further investigate the mechanism of CC@NMO energy storage, there is a need to analyze the microstructure of the material. By analyzing the SEM, XRD, FTIR, and XPS patterns of the CC@NMO, it is possible to obtain the micro-schematic diagram shown in Figure 8, which reveals the storage mechanism of NMO [55]. The ion pre-intercalation influences the electrochemical behavior of MnO₂ basically through the following three points. Firstly, the pre-intercalated ions can accelerate the diffusion kinetics of MnO₂-based materials. The guest ions pre-intercalated into the interlayer structure will expand the interlayer spacing to provide more ion diffusion channels [56]. Meanwhile, the constituent water molecules can reduce the effect of the positive ion electrostatic repulsion to accelerate charge and ion transfer [33,57]. Secondly, ion pre-intercalation can stabilize the structure of MnO₂. Relevant studies have proved that NH_4^+ ions provide structural support for the electrode material as structural columns [35,58]. Thirdly, ion pre-intercalation can switch the electrochemical behavior of MnO_2 into that of a supercapacitor. When ions are pre-intercalated into MnO2, the average Mn oxidation state will be reduced, and Mn³⁺/Mn⁴⁺ redox coupling occurs. More metal ions can be involved in the redox reaction, which makes for a larger pseudo-capacitance. The MnO_2 will be just like the following equation: $M_xMnO_2 \Leftrightarrow MnO_2 + xM^+ + xe^-$ (M⁺ = H⁺, Na⁺, K⁺, NH₄⁺). The CV curves of ion-pre-intercalated MnO_2 will increase by a couple of redox peaks [25]. All of the above are consistent with the electrochemical test of CC@NMO//AC. Overall, NH_4^+ ion pre-intercalation enhances the electrochemical behavior of the CC@NMO electrode and improves the energy density of ASCs.



Figure 8. Schematic illustration of CC@NMO.

4. Conclusions

In conclusion, we successfully synthesized a $MnO_2/carbon cloth$ electrode with NH_4^+ ions pre-intercalated by a one-step hydrothermal method. Compared with the CC@MnO₂ electrode, the CC@NMO electrode obviously has a wider potential window, as well as a larger specific capacity. The pre-intercalation of NH₄⁺ ion increases the upper limit of the stable working potential window of the electrode from 0.8 V to 1.1 V, and the capacitance can reach 181.4 F g^{-1} at 0.5 A g^{-1} . Our improvement of the CC@NMO electrode provides strong support for the high energy density of ASCs. After capacitance matching with an AC electrode, the CC@NMO electrode was fabricated into an ASC. When operating at 1 A g^{-1} , the capacitance of the CC@NMO//AC is up to 126.63 F g^{-1} . Notably, it still remains at 61.8 F g^{-1} when the current density rises to 20 A g^{-1} . Through a Ragone plot, one can see that the energy density of the CC@NMO//AC can reach 63.49 Wh kg⁻¹, and the power density can also be up to 949.8 W kg⁻¹ at 1A g⁻¹. Meanwhile, the pre-intercalation of NH_4^+ also significantly enhances the cycling stability. After completely cycling for 10,000 times at 10 A g^{-1} , the device still has 81% capacitance retention. The improvement of the stability and energy density of CC@NMO comes from pre-intercalation with NH₄⁺ ions, which form supportive structures in the interlayer of MnO₂. Moreover, the NH₄⁺ ions accelerate charge and ion transfer by enlarging the spacing between layers. Thus, the constructive role of the ammonium ion pre-intercalation technique in improving the electrochemical performance of $MnO_2/carbon$ cloth electrodes has been demonstrated. This work could prove to be an innovative contribution that helps in increasing the energy density of asymmetric supercapacitors.

Supplementary Materials: The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/ma17081858/s1. Figure S1: (a) TEM image of CC@NMO, (b) HRTEM image of CC@NMO; Figure S2: XRD patterns of CC@NMO, CC@MnO₂, and CC; Figure S3: EIS curves of CC@NMO and CC@MnO₂; Figure S4: (a) Comparison of CC@NMO and CC@MnO₂ at 1 mV s⁻¹ at 0–1.1 V and (b) GCD curves of CC@MnO₂ at 0–0.8 V at different current densities; Figure S5: Cycle stability of CC@NMO at 5 A g⁻¹; Figure S6: (a) GCD curves of AC at –0.1 to –1.1 V at different current densities and (b) capacitance of CC@NMO and AC at different current densities; Figure S7: Comparison of cycle stability of CC@NMO//AC and CC@MnO₂//AC; Table S1: Comparison of energy density and power density with other recent studies.

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