Aqueous supercapacitors show advantages of high safety, prolonged lifespan, and low cost, etc. but there have never been commercial market products, nor quantitative investigation of practical pouch devices of aqueous supercapacitors. Herein, to achieve their lab-scale to real-life manufacture, a unique MoO$_x$ for supercapacitor use is constructed by a hydrothermal and annealing strategy suitable for industrialization, which plays three key functions, including precisely adjusted interlayer spacing, conductive flexible graphite carbon and abundant oxygen vacancies. As a result, the as-synthesized electrode yields an ultra-high specific capacitance of 717 F g$^{-1}$ at 1 A g$^{-1}$ and ultra-long cycling durability with no obvious capacitive loss even after 100 000 cycles. Realistically, the assembled asymmetric supercapacitor (MoO$_x$-HDA-3//MnO$_2$) exhibits extraordinary energy density of 78.2 Wh kg$^{-1}$, superior to many advanced supercapacitors reported to date. We have fabricated pouch devices, which can successfully run 3C products such as tablets and smartphones, and maintain stable electrochemical performance even after heavy strikes, fires, and pressures. Quantitative investigation results confirm that the pouch device delivers an excellent specific capacitance of 74.7 F g$^{-1}$ and a high energy density of 41.5 Wh kg$^{-1}$. This work enhances the confidence of pushing aqueous supercapacitors to realistic energy storage market.

1. Introduction

Pouch devices, as an encapsulating technology for battery-type energy storage devices, include many advantages such as higher safety, lighter weight, and more flexible size adjustment.$^{[1-3]}$ Compared with the traditional metal shell battery, the pouch device's energy density can be increased by 20–50%; the cycle attenuation can also be reduced by 7%. More meaningfully, if the battery is stimulated to explode, the pouch device can effectively relieve the internal high pressure to mitigate the explosion. In recent years, many new energy vehicles such as Buick’s Blue 6, Chevrolet’s Bolt, and Nissan’s Leaf, have introduced pouch encapsulating technology in the development of high-energy batteries. This undoubtedly confirms the vast potential of pouch devices for practical applications and commercialization. Fortunately, these have also been reported in the field of supercapacitors.

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in recent years. Scorsone et al. synthesized a porous diamond-coated polypyrrole electrode by plasma vapor chemical deposition and encapsulated the pouch device with TEABF4 as the electrolyte.\[^{[6]}\] A novel pouch device using Pd nanoparticles acts as the active material and ionic liquid as the electrolyte was successfully encapsulated to collect the energy generated by a wind turbine.\[^{[7]}\] Without exception, most pouch devices rely on expensive and dangerous organic/inorganic solutions or ionic liquids as electrolytes, which run counter to the pursuit of low-cost, highly safe commercialization requirements.\[^{[8–10]}\] Therefore, the development of a pouch device using an aqueous solution as the electrolyte could be commercially significant.

Molybdenum oxide combines excellent physicochemical properties such as high specific capacitance, low cost, natural abundance, and environmental friendliness, so it is regarded as an ideal electrode material for supercapacitors.\[^{[9–11]}\] Recently, Down et al. optimized the nucleation conditions of MoO\(_3\) on the G/AME surface to assemble a MoO\(_2\)-G/AME symmetric supercapacitor with a specific capacitance up to 1212 F g\(^{-1}\).\[^{[12]}\] Zhou synthesized MoO\(_3\) nanoflakes with a length of 200\(\mu\)m using an improved hydrothermal reaction, which achieved a specific capacitance of 1198 F g\(^{-1}\) at 2 mV s\(^{-1}\).\[^{[13]}\] An in situ N doping strategy for low-valence-state Mo is reported to synthesize N-MoO\(_x\)-HDA with a volume specific capacitance of up to 4100 mF cm\(^{-2}\) at 0.25 mA cm\(^{-2}\).\[^{[14]}\] As a guest intercalator, alkylamines, with their easy-to-control chain length, can be carbonized to form a conductive layer, while reducing carbon can further enrich the valence composition of the host MoO\(_3\). A few alkylamine intercalated MoO\(_3\) have been studied for supercapacitive metal oxides, thereby opening up new innovations for high-energy aqueous supercapacitors.

2. Results and Discussions

2.1. Electrode Preparation and Characterization

Alkylamine-tuned MoO\(_3\) is prepared via a simple hydrothermal method and intercalation strategy as shown in Figure 1a. First, a facile hydrothermal reaction was used to generate the host compound MoO\(_3\) with a plate-like structure. Second, the obtained plate-like MoO\(_3\) is inserted into the interlayer with alkylamines to realize the expansion of the interlayer spacing. Then the intercalated alkylamine is carbonized, causing the surface of MoO\(_3\) to be coated with highly conductive graphitic carbon while generating a large number of oxygen vacancies. The detailed mechanism of alkylamine-tuned MoO\(_3\) during different fabrication periods is discussed in the Section 2.3.

Scanning electron microscope (SEM) details the morphological changes of as-prepared samples at different stages. The untreated MoO\(_3\) showed a single sheet structure with a width of 1–1.4\(\mu\)m, while the length was 2–3\(\mu\)m (Figure 1b). During the annealing process, high temperature will destroy the host structure of MoO\(_3\), so the annealed MoO\(_3\) presents a scattered flake structure with a radius of about 0.25\(\mu\)m, as illustrated in Figure 1c. Compared with pure MoO\(_3\), the alkylamine-tuned MoO\(_3\)-HDA-3 exhibits a dense porous structure, shown in Figure 1d, which is necessary for the migration of electrolyte ions inside the electrode. Furthermore, there is a significant difference in the BET surface area of MoO\(_3\) (2.99 m\(^2\) g\(^{-1}\)) and MoO\(_3\)-HDA-3 (24.28 m\(^2\) g\(^{-1}\)), as shown in Figure S1. Supporting Information. This may be due to the enlarged interlayer spacing and abundant pore structure. The uniform distribution of O, Mo, and C elements in MoO\(_3\)-HDA-3 can be observed by energy dispersive X-ray spectroscopy (EDS) mapping, presented in Figure 1e–h, and EDS spectra, shown in Figure S2. Supporting Information, demonstrating the perfect combination of MoO\(_3\) and alkylamine. The microscopic alterations between MoO\(_3\) and MoO\(_3\)-HDA-3 are further revealed by using a transmission electron microscope (TEM). At the interface of MoO\(_3\), the as-prepared pure MoO\(_3\) shows a set of regular parallel layers with a lattice spacing of 0.329 nm, displayed in Figure 1i, which corresponds well to the (021) lattice plane of MoO\(_3\) at 2\(\theta\)=27.2\(^\circ\), confirming the successful synthesis of host compound MoO\(_3\) (JCPDS: 76–1003). The TEM image of MoO\(_3\)-HDA-3 reveals a large number of pore structures as shown in Figure 1j, which is consistent with Figure 1d. Additionally, the graphitic carbon layers with excellent conductivity are observed in Figure 1j,
which is crucial to improve the energy storage performance of active materials. Selected area electron diffraction pattern, shown in Figure 1k, with clear diffusive rings confirms that MoO<x>3-HDA-3 is a typical polycrystal. Thus, based on TEM and SEM analysis, this three-in-one alkylamine-tuned strategy can positively affect the microstructure of MoO<x>3.

2.2. Improvement of Electrochemical Property of MoO<x>3

To evaluate the superiority of the alkylamine-tuning strategy, we focused on comparing the electrochemical performance of pure MoO<x>3 and MoO<x>-HDA-3 in a three-electrode system containing 5 mM LiCl electrolyte with saturated calomel electrode (SCE) reference electrode and carbon cloth counter electrode. The cyclic voltammetry (CV) curves collected from pure MoO<x>3 and MoO<x>-HDA-3 electrodes at 10 mV s<sup>-1</sup> are reported in Figure 2a. A very meaningful enhancement of current density was found after pure MoO<x>3 was tuned by hexadecylamine, due to the enlarged interlayer spacing resulting in an enlarged ion accessible surface area, the lower electrolyte adsorption energy promoted by oxygen vacancies, and the extraordinary conductivity of interlayer graphitic carbon. The galvanostatic charge–discharge (GCD) curves of pure
MoO$_3$ and MoO$_x$-HDA-3 electrodes at different current densities are recorded in Figure 2b,c. Compared with pure MoO$_3$, MoO$_x$-HDA-3 electrode achieves increased charge–discharge time under the same current density, showing better electrochemical storage performance, which is highly consistent with the conclusion of Figure 2a. Compared to previously reported Mo-based capacitors,[17–19] our synthesized alkylamine-tuned MoO$_x$ exhibit a stably high potential window of −1 to 0.5 V versus SCE. This can be attributed to the introduction of oxygen vacancies, which can effectively reduce the adsorption energy of active materials to electrolyte ions, and further increase the transfer charge flux required for the redox reaction, achieving a higher voltage window.[8] Figure 2d calculates the detailed specific capacitance and Coulombic efficiency of MoO$_x$-HDA-3 at various current densities. It is worth noting that MoO$_x$-HDA-3 reveals the largest specific capacitance (717 F g$^{-1}$), which is about 30 times higher than that of pure MoO$_3$ (23.3 F g$^{-1}$)[20,21] and surpasses most advanced electrodes (Figure 2e and Table S1, Supporting Information[22–37]). Additionally, the Coulombic efficiency of MoO$_x$-HDA-3 shows an upward trend with the increase of the current density, and the maximum Coulombic efficiency is 99.7% when the current density is 10 A g$^{-1}$.

The Faradaic reaction of alkylamine-tuned MoO$_x$ in LiCl aqueous electrolyte involves the surface adsorption–desorption of Li$^+$ (Equation (1)) and the internal intercalation/de-intercalation of Li$^+$ (Equation (2)).[10,38] In order to further elucidate the charge storage mechanism of alkylamine-tuned MoO$_x$, the ratio of capacitive charge storage and diffusion-controlled insertion processes was calculated according to the Dunn’s method. Figure 2f presents the capacitance and diffusion contribution ratios for MoO$_x$-HDA-3 at various scan rates. Specifically, at 0.5 mV s$^{-1}$, MoO$_x$-HDA-3 shows a higher proportion of capacitive contribution of 62.6% (>50%), which can be considered as a capacitor-type material. The capacitive contribution ratios of MoO$_x$-HDA-3 is positively correlated with the scan rate.

Figure 2. a) CV curves of pure MoO$_3$ and MoO$_x$-HDA-3 electrodes measured at 10 mV s$^{-1}$. b) GCD curves of MoO$_3$ and MoO$_x$-HDA-3 electrodes measured at various current densities. c) GCD curves of MoO$_x$-HDA-3 electrode measured at 1–10 A g$^{-1}$. d) Coulombic efficiency and specific capacitance of MoO$_x$-HDA-3 measured at different current densities. e) Specific capacitance of MoO$_x$-HDA-3 electrode in comparison with other reported electrodes. f) Capacitance contribution of MoO$_x$-HDA-3 collected at various scan rates. g) Cycling stability of MoO$_3$ and MoO$_x$-HDA-3 electrodes in 5 m LiCl at 100 mV s$^{-1}$. © 2022 The Authors. Advanced Functional Materials published by Wiley-VCH GmbH
rate (64.5% at 1 mV s⁻¹, 70.3% at 2 mV s⁻¹, 77.2% at 4 mV s⁻¹), indicating the excellent energy storage capability of alkylamine-tuned MoOₓ at high current densities.

\[
\text{(MoO}_x\text{)}_{\text{surface}} + \text{Li}^+ + \text{e}^- \leftrightarrow \text{(MoO}_x\text{Li)}_{\text{surface}} \tag{1}
\]

\[
\text{MoO}_x + y\text{Li}^+ + y\text{e}^- + z\text{H}_2\text{O} \leftrightarrow \text{Li}_y(\text{H}_2\text{O})_z(\text{MoO}_x)^y^+ \tag{2}
\]

Furthermore, after 100 000 cycles (100 mV s⁻¹ in 5 M LiCl), MoOₓ-HDA-3 shows a remarkable capacitance retention of 98% (Figure 2g), indicating a superior electrochemical long-term cycling stability, which is significantly better than pure MoOₓ electrode. In order to explore the cause of ultralong cycle stability, we performed XPS and TEM tests on the MoOₓ-HDA-3 electrodes after 100 000 cycles. The XPS spectrum is roughly the same as before the cycle (Figure S3, Supporting Information), and the proportion of Mo⁶⁺ (32.8%), Mo⁵⁺ (23.5%), and Mo⁴⁺ (43.7%) does not change significantly, verifying the excellent electronic structure stability of MoOₓ-HDA-3 electrode. Meanwhile, the graphitic carbon coated on MoOₓ-HDA-3 after 100 000 cycles can still be found by TEM (Figure S4, Supporting Information), which can effectively offset the stress released during multiple electrochemical charge/discharge and ensure the integrity of the microstructure. The stable electronic structure and the flexible graphitic carbon work together to safeguard the ultralong cycle stability of MoOₓ-HDA-3 electrode. As far as we know, it is the optimal value currently known for Mo-based electrodes for supercapacitors (Table S1, Supporting Information).

The gratifying electrochemical performance can be explained in three ways: first, guest alkylamine molecules follow the interlayer tunnel along the interlayer of the layered host compound.
MoO₃, resulting in the expansion of interlayer spacing, which is conducive to the rapid transmission of ions in the layered host and promotes energy storage performance that rely on surface electrochemical reactions. Then, the graphitic carbon coated on MoOₓ-HDA-3 can not only entirely enhance the conductivity of the active material, but also effectively alleviate the volume expansion of the electrode during electrochemical charge/discharge, resulting in ultralong cycle durability. Finally, abundant oxygen vacancies promote interaction between electrodes and electrolyte ions by reducing the Bader charge of adjacent O atoms to further enhance the utilization of active materials.

2.3. Alkylamine-Tuning Mechanism

To understand the influence mechanism of intercalant with different chain length on the host compound MoO₃, we selected three kinds of alkylamines: butylamine, dodecylamine, and hexadecylamine as intercalants for in-depth study. The CV and GCD curves of MoOₓ-Ba-3, MoOₓ-DDA-3, and MoOₓ-HDA-3 electrodes are displayed in Figure 3a, and the rest are given in Figures S5–S7, Supporting Information. The CV curves of MoOₓ-HDA-0.5, MoOₓ-HDA-1, MoOₓ-HDA-3, and MoOₓ-HDA-5 electrodes (Figure 3a) maintain an ideal rectangular-like shape at 10 mV s⁻¹, due to the continuous Faraday redox reaction of Mo⁴⁺/Mo⁵⁺/Mo⁶⁺ and the highly reversible intercalation–deintercalation of Li⁺. As the chain length of the intercalant increases, the corresponding current density also shows a rising trend. The GCD curves of MoOₓ-HDA-0.5, MoOₓ-HDA-1, MoOₓ-HDA-3, and MoOₓ-HDA-5 electrodes at 1 A g⁻¹ are showed in Figure 3b. Obviously, the discharge time is positively correlated with the chain length of the intercalant, which is highly consistent with the phenomenon in Figure 3a. This may be because as the...
alkylamine chain length increases, the interlayer spacing gradually expands, which can provide more accessible active sites for the electrolyte ion, resulting in enhanced energy storage performance. Moreover, Figure 3c details the specific capacitance of pure MoO₃, MoOₓ⁻ₓBA-3, MoOₓ⁻ₓDDA-3, and MoOₓ⁻ₓHDA-3 electrodes calculated based on the GCD curves. The MoOₓ⁻ₓBA-3, MoOₓ⁻ₓ-DDA-3 and MoOₓ⁻ₓ-HDA-3 electrodes all yielded enhanced specific capacitance, while the pure MoO₃ electrode is indeed extremely small, revealing that the alkylamine-tuned strategy can effectively enhance the energy storage performance of pure MoO₃. The Nyquist curves of MoOₓ⁻ₓBA-3, MoOₓ⁻ₓ-DDA-3, and MoOₓ⁻ₓ-HDA-3 are presented in Figure S8, Supporting Information, to further explore the resistance response. Compared with MoOₓ⁻ₓBA-3 and MoOₓ⁻ₓ-DDA-3, MoOₓ⁻ₓ-HDA-3 shows the smallest semicircle, indicating the lowest charge transfer resistance. The magnitude of Z'-intercept represents the equivalent series resistance, which includes the minimum resistance of 0.39 Ω for MoOₓ⁻ₓ-HDA-3, 8.67 Ω for MoOₓ⁻ₓ-BA-3, and 3.50 Ω MoOₓ⁻ₓ-DDA-3.

X-ray diffraction (XRD) was chosen to further analyze the structural changes of pure MoO₃ before and after intercalation with alkylamines. As shown in Figure 3d, obviously, the host compound MoO₃ exhibits multiple strong reflection peaks that are highly consistent with typical MoO₃ (ICPDS: 76-1003), which suggested the d_{200} = 0.69 nm interlayer spacing at 2θ = 12.77°. When the alkylamine is inserted into the pure MoO₃, the diffraction peaks are mainly concentrated at low angles (5°–20°), and the diffraction angle on the lattice plane of (020) is reduced from 12.77° to 6.78°, which confirms that the interlayer spacing has been expanded from 0.69 to 1.31 nm (according to the Bragg’s formula).[39] High-temperature carbonization promotes the typical polycrystalline structure of MoOₓ⁻ₓ-HDA-3, which shifts the diffraction peak at (020) to 2θ = 75°, and the interlayer spacing is calculated to be 1.19 nm.[40] This shrinkage of the interlayer spacing may be explained as the collapse of the intercalation structure induced by the carbonization of the alkylamine. Figure 3e,f reports the XRD patterns of MoOₓ⁻ₓ-BA-3, MoOₓ⁻ₓ-DDA-3, MoOₓ⁻ₓ-HDA-3, and the corresponding interlayer spacing at (020) lattice spacing, respectively. It is thus easy to perceive that the interlayer spacing of intercalated MoO₃ will increase significantly as the chain length of the intercalator becomes longer, which shows practical significance for the synthesis of MoO₃ with adjustable interlayer spacing.

In light of the importance of rich valence states to the energy storage performance of active materials, we collected the XPS spectra of MoOₓ⁻ₓ-BA-3, MoOₓ⁻ₓ-DDA-3, and MoOₓ⁻ₓ-HDA-3 and displayed them in Figure 3g–i (the pure MoO₃ is given in Figure S9, Supporting Information). In the Mo 3d spectrum, these fitting peaks located at 232.6 and 235.6 eV can be attributed to the 3d_{5/2} and 3d_{3/2} of Mo⁶⁺, respectively.[26] Since Mo⁶⁺ may be partially reduced during carbonization, the low-valence fitting peaks of Mo⁵⁺ and Mo⁴⁺ appear in the Mo 3d spectrum. The fitting curves at 231.3 and 234.5 eV are ascribed to 3d_{5/2} and 3d_{3/2} of Mo⁵⁺, while the two fitting curves at 229.5 and 233.7 eV are ascribed to 3d_{5/2} and 3d_{3/2} of Mo⁴⁺, respectively.[41] To further explain the evolution mechanism of various chain length intercalants to the valence states of Mo atoms, the percentage values of Mo atoms with different valence states in the Mo 3d spectrum were calculated and recorded in Table S2, Supporting Information, (calculated by the integral area). As reported in Table S2, Supporting Information, the percentage of Mo⁵⁺ in pure MoO₃ is almost 0%, but with the introduction of alkylamines, the proportion of Mo⁵⁺ increases significantly, indicating the formation of abundant oxygen vacancies. The O 1s XPS spectra also can strongly prove the existence of oxygen vacancies. For MoO₃, only one peak attributed to Mo–O is found at 529.8 eV (Figure S10, Supporting Information). However, MoOₓ⁻ₓ-HDA-3 fitted three peaks at 529.8, 531.4, and 532.7 eV (Figure S11, Supporting Information), which were assigned to Mo–O, oxygen vacancies and –OH, respectively, revealing the existence of oxygen vacancies.[42] Oxygen vacancies of MoO₃ can not only promote the adsorption of Li⁺ by reducing the Bader charge of adjacent O atoms, but also decrease the band gaps increasing conductivity. When butylamine, dodecylamine, and hexadecylamine are selected as intercalants, the corresponding Mo⁴⁺ ratios are 13.7%, 22.5%, and 34%, respectively. Compared with Mo⁴⁺, Mo⁵⁺ exhibits higher conductivity and more active electrochemical characteristics,[10] which can also reasonably explain the superior energy storage performance of MoOₓ⁻ₓ-HDA-3.

The feed ratio of alkylamine during the turn reaction was found to have a profound influence on the energy storage performance of the as-synthesized electrode. Figure 4a,b represents the CV and GCD curves of electrodes as-prepared with various hexadecylamine ratios (the rest are given in Figures S12–S14, Supporting Information), and the precise specific capacitance values are listed in Figure 4c. As the alkylamine to MoO₃ molar ratio increases from 0.5 to 5, the specific capacitance of MoOₓ⁻ₓ-HDA-n increases steadily along with the increase ratio of alkylamine to MoO₃ and reaching the maximum at n = 3, followed by a slight decrease (n = 5), which can be explained from two aspects. On the one hand, the interlayer spacing of the as-prepared electrode expands with the increase of the alkylamine ratio, resulting in a larger ion accessible surface area. Then, as the ratio of alkylamine continues to increase (n = 5), the flexible alkyl chains of the intercalant entangle with each other during the intercalation process, which severely weakens the intercalation effect to the layered host, causing worse electrochemical performance. On the other hand, the alkylamine ratio is closely related to the graphitic carbon content of the active material after carbonization. Appropriate alkylamine ratio can effectively increase the content of graphitic carbon in the active material and optimize the electrical conductivity and cycle durability. However, an excessive ratio will increase the thickness of the graphitic carbon layer on the surface of MoO₃, which can hinder the contact between the electrolyte and pseudocapacitive MoO₃, and further reduce the electrochemical performance. To explore the kinetics of as-prepared electrodes, EIS was chosen to test the Nyquist curves of MoOₓ⁻ₓ-HDA-0.5, MoOₓ⁻ₓ-HDA-1, MoOₓ⁻ₓ-HDA-3, and MoOₓ⁻ₓ-HDA-5. As reported in Figure 4d, in the low frequency region, the impedance spectra of all electrodes are observed to be close to a vertical straight line, which indicates good capacitance characteristics. The equivalent series resistance of the as-prepared electrode can be obtained by the intersection of the impedance spectrum and the Z’-axis in the high frequency region. Benefiting from the expanded interlayer spacing and abundant pore structure, the equivalent series resistance...
of MoO₅-HDA-3 is only 0.39 Ω, which is much smaller than 1.10 Ω for MoO₅-HDA-0.5, 1.08 Ω for MoO₅-HDA-1, and 1.13 Ω for MoO₅-HDA-5, demonstrating the excellent conductivity.

The XRD patterns of electrodes prepared with different intercalant ratios are shown in Figure 4e. Except for the broad peaks of the coated graphitic carbon, the clear diffraction peaks observed at 2θ values of 10.8°, 9.9°, 7.5°, and 10.1° can all be successfully normalized to the (020) lattice plane of host compound MoO₃, which indicates that the alkylamine-tuned strategy in this work is well implemented. The interlayer spacing of the corresponding sample at (020) is accurately calculated and shown in Figure 4f. It is noteworthy that with the increase in the ratio of hexadecylamine, the change trend of the interlayer spacing is not an ideal linear relationship. Briefly, with the increase of the molar ratio of alkylamine to pure MoO₃, the maximum interlayer spacing was achieved at n = 3, and then it decreased significantly. This may be explained by the fact that more intercalant can promote a more thorough intercalation reaction, but then as the ratio of intercalant continues to increase, the flexible alkyl chains entangle with each other during the intercalation process, resulting in worse intercalation efficiency. Figure 4g–i shows the Mo 3d spectra of MoO₃-HDA-0.5, MoO₃-HDA-1, and MoO₃-HDA-5, which contain six fitting peaks of Mo⁶⁺ 3d₃/₂ (235.6 eV), Mo⁵⁺ 3d₅/₂ (235.6 eV), Mo⁵⁺ 3d₃/₂ (231.3 eV), Mo⁵⁺ 3d₃/₂ (234.5 eV), Mo⁴⁺ 3d₃/₂ (229.5 eV), and Mo⁴⁺ 3d₃/₂ (233.7 eV). Table S2, Supporting Information, records the percentages of Mo⁶⁺, Mo⁵⁺, and Mo⁴⁺ atoms of pure MoO₃, MoO₃-HDA-0.5, MoO₃-HDA-1, MoO₃-HDA-3, and MoO₃-HDA-5. For pure MoO₃, the content of Mo⁵⁺ (or Mo⁴⁺) is extremely low, and most Mo atoms are present as Mo⁶⁺, but MoO₃-HDA-0.5, MoO₃-HDA-1, MoO₃-HDA-3, and MoO₃-HDA-5 generate a large amount of Mo⁴⁺ and Mo⁵⁺ due to the reducibility of alkylamines after carbonization. The decrease in the relative content of Mo⁶⁺ indicates the formation of more oxygen vacancies, which is essential for enhancing the conductivity and adsorption to electrolyte ions. Compared with others, the total content of Mo⁵⁺ and Mo⁴⁺ (oxygen valence) in MoO₃-HDA-3 is the highest, and the rich oxygen valence is indispensable for the improvement of electrochemical performance.

2.4. Oxygen Vacancy Strengthening Mechanism

The adsorption energy of the as-prepared electrode for electrolyte ions is closely related to the electrochemical storage performance. To investigate the influences of oxygen vacancy on the Li⁺ adsorption, MoO₃ with single and double oxygen vacancy were investigated. There are different oxygen vacancy sites for single/double oxygen vacancy MoO₃. The structures with the lowest energy are shown in Figure 5a–c with key bond lengths listed in Table S3, Supporting Information. Compared with pristine MoO₃, the molecular structure of single oxygen vacancy MoO₃ does not have obvious change. However, the molecular structure of double oxygen vacancy MoO₃ has conspicuous alteration with the breakage of Mo–O bond and changes of the oxygen atom position. Single and double oxygen site vacancies both change the Mo–Mo and O–O distances, nevertheless, double oxygen vacancy MoO₃ leads to longer Mo–Mo and O–O distances changes than that of single oxygen vacancy MoO₃.

The most stable complex for lithium adsorption on pristine and single/double vacancy MoO₃ is depicted in Figure 5d–f with Li–O lengths listed in Table S4, Supporting Information. Li⁺ is adsorbed on the bridge site between two oxygen atoms for pristine and single oxygen vacancy MoO₃, resulting in two Li–O bonds. The shorter Li–O bond lengths for Li adsorption on single O vacancy MoO₃ than pristine MoO₃ suggests that

Figure 5. Optimized structures of a) pristine MoO₃, b) single O vacancy MoO₃, and c) double O vacancy MoO₃. Lithium adsorption on d) pristine MoO₃, e) single O vacancy MoO₃, and f) double O vacancy MoO₃. g) Calculated adsorption energy of Li on pristine and single/double O vacancy MoO₃.
single oxygen vacancy promotes the adsorption of $\text{Li}^+$. With regards to double oxygen vacancy MoO$_3$, $\text{Li}^+$ forms bonds with three O atoms, indicating that $\text{Li}^+$ has stronger interactions with double oxygen vacancy MoO$_3$ than that with pristine and single oxygen vacancy MoO$_3$. The adsorption energy follows the order of pristine MoO$_3$ > single O vacancy MoO$_3$ > double O vacancy MoO$_3$ (Figure 5g), further confirming that the presence of oxygen vacancy could promote the adsorption of $\text{Li}^+$.

Electron density differences analysis were also conducted to explore the adsorption mechanism. It is shown in Figure 6a–c that the $\text{Li}^+$ loses electrons whereas O atom gains electrons when $\text{Li}^+$ is adsorbed by MoO$_x$. Moreover, electrons are depleted between O and Mo atoms. According to the Bader charge analysis (Table S5, Supporting Information), the Bader charge of O atoms connecting with $\text{Li}^+$ are smaller for single and double oxygen vacancy MoO$_x$ compared with pristine MoO$_3$, therefore, the O atoms in single/double oxygen vacancy MoO$_3$ have a higher tendency to attract $\text{Li}^+$ atoms. Based on the above discussion, it is concluded that the oxygen vacancy could decrease the Bader charge of adjacent O atoms, promoting the interactions between $\text{Li}^+$ and MoO$_x$.

Total density of states and projected density of states analysis were conducted with results shown in Figure 6d–f. The pristine MoO$_3$ had a larger band gap than single/double oxygen vacancy MoO$_x$. In addition, the oxygen vacancy could induce a shift from conduction band to valence band. The Fermi level is at the conduction band for single/double oxygen vacancy MoO$_x$. With the removal of one or two O from MoO$_3$, the Mo$^{6+}$ will be reduced to Mo$^{5+}$ or Mo$^{4+}$ to maintain the neutral charge of the material. Hence, the d orbital of Mo will be partially filled with electrons, leading to the increase of the conduction of MoO$_x$. Moreover, the band gap as well as the location of Fermi level suggest that oxygen vacancy can increase the conductivity of MoO$_3$. The band structure analysis also confirms that single/double oxygen vacancy MoO$_3$ has smaller band gap than pristine MoO$_3$ (Figure 6g–i). Therefore, the charge transfer of single/double oxygen vacancy MoO$_3$ will be promoted. The higher electronic conductivity as well as electron transfer facilitates $\text{Li}^+$ adsorption and diffusion, increasing $\text{Li}^+$ storage performance.
Based on the above results, oxygen vacancy promotes the Li\(^+\) adsorption on MoO\(_x\). The adsorption energy of Li\(^+\) follows the order of double oxygen vacancy MoO\(_x\) < single oxygen vacancy MoO\(_x\) < pristine MoO\(_3\). When Li\(^+\) adsorbs on MoO\(_x\), it forms bonds with O atoms with Li\(^+\) losing electrons and O obtaining electrons. Moreover, oxygen vacancy increases the conductivity of MoO\(_3\) by decreasing the band gaps and moving Fermi level into the conduction band. In addition, the electron transfer will also be promoted. Overall, the oxygen vacancy will promote Li\(^+\) adsorption and diffusion in MoO\(_x\), which is necessary for the synthesis of high-energy-density supercapacitor electrodes.

2.5. Asymmetric Supercapacitors and Real-Life Pouch Devices

Relying on the as-prepared MoO\(_x\)-HDA-3 as the anode, MnO\(_2\) as the cathode, and 5 m LiCl as the electrolyte, an asymmetric supercapacitor (ASC) was assembled successfully, denoted as MoO\(_x\)-HDA-3//MnO\(_2\). To balance the charge of the anode and cathode, we adjusted the corresponding mass load and tested the CV curves in 5 m LiCl. Evidently, MoO\(_x\)-HDA-3 contributes an effective anode potential of −1 to 0 V, and MnO\(_2\) provides an effective cathode potential of 0–1 V, which ensures a stable 2 V voltage window for the ASC (Figure 7a). The CV curves of the ASC in different voltage windows are displayed in Figure 7b, indicating that its maximum working potential window can reach 2 V. Figure 7c presents the CV curves of the ASC in the 2 V high voltage window. The shape of the CV curves does not appear to be obviously distorted due to the increase of the scan rates, indicating its excellent rate performance. Similar symmetrical GCD curves of the assembled ASC at various current densities were collected and recorded in Figure 7d. The calculation results show that the assembled ASC exhibits an ultrahigh specific capacitance

![Figure 7](https://example.com/image7.png)

Figure 7. a) CV curves of the anode (MoO\(_x\)-HDA-3) and cathode (MnO\(_2\)) in a three-electrode cell. b) CV curves of the MoO\(_x\)-HDA-3//MnO\(_2\) device tested in different potential windows at a scan rate of 10 mV s\(^{-1}\). c) CV curves of MoO\(_x\)-HDA-3//MnO\(_2\) device collected at various scan rates. d) GCD curves of MoO\(_x\)-HDA-3//MnO\(_2\) device collected at various current densities. e) Ragone plots of MoO\(_x\)-HDA-3//MnO\(_2\) device and others reported device. f) Cycling stability of MoO\(_x\)-HDA-3//MnO\(_2\) device measured at 100 mV s\(^{-1}\). g) Specific capacitance of flexible all-solid-state ASC device collected at various current densities. h) Capacitance retention of the flexible all-solid-state ASC device collected at different bend angles. i) Capacitance retention under repeated mechanical deformations at bending angle of 90°.
of 141 F g\(^{-1}\) at 0.3 A g\(^{-1}\) (Figure S15, Supporting Information), which is crucial for the improvement of energy density (according to equation \(E = \frac{1}{2}CV\)).

Energy density (\(E\)) and power density (\(P\)) are two crucial indicators for appraising the practicability of ASC. Figure 7e shows the Ragone plot of the assembled MoO\(_2\)-HDA-3//MnO\(_2\) device compared with other recently reported representative devices. It is noteworthy that the MoO\(_2\)-HDA-3//MnO\(_2\) device presents an ultrahigh energy density of 78.2 Wh kg\(^{-1}\) at 300 W kg\(^{-1}\) and 30.4 Wh kg\(^{-1}\) at 3172 W kg\(^{-1}\), which is better than most of the recently reported devices, for example, RuO\(_2@\)COF (23.3 Wh kg\(^{-1}\), 261 W kg\(^{-1}\)),\(^{[46]}\) Bi\(_2\)Se\(_3@\)CoO\(_{0.85}\)Se (30.9 Wh kg\(^{-1}\), 559 W kg\(^{-1}\)),\(^{[47]}\) NiCoP@GO (32.9 Wh kg\(^{-1}\), 1301 W kg\(^{-1}\)),\(^{[48]}\) C-GMOF@AC (30.3 Wh kg\(^{-1}\), 137 W kg\(^{-1}\)),\(^{[49]}\) LDH-NF@VG (56.8 Wh kg\(^{-1}\), 260 W kg\(^{-1}\)),\(^{[50]}\) Ni\(_3\)Se\(_2@\)AC (38.4 Wh kg\(^{-1}\), 794.5 W kg\(^{-1}\)),\(^{[51]}\) CoP@FeP\(_4\) (46.3 Wh kg\(^{-1}\), 695 W kg\(^{-1}\)),\(^{[52]}\) MXene@CNT-HQ (62 Wh kg\(^{-1}\), 281 W kg\(^{-1}\)),\(^{[53]}\) MnO\(_2@\)GO@CGO (31.8 Wh kg\(^{-1}\), 453 W kg\(^{-1}\)),\(^{[54]}\) Li\(_3\)Ti\(_2\)O\(_6@\)NGO (26.2 Wh kg\(^{-1}\), 799 W kg\(^{-1}\)),\(^{[55]}\) NNC-01@AC (43.02 Wh kg\(^{-1}\), 840.3 W kg\(^{-1}\)),\(^{[56]}\) rGO@Ni@P (41.66 Wh kg\(^{-1}\), 1200 W kg\(^{-1}\)),\(^{[57]}\) and RGO@Mn\(_3\)O\(_4\) (23.5 Wh kg\(^{-1}\), 990 W kg\(^{-1}\)).\(^{[58]}\) More importantly, at 100 mV s\(^{-1}\), 97% specific capacitance of the assembled MoO\(_2\)-HDA-3//MnO\(_2\) device is retained after 30 000 cycles, which indicates a practical long-cycle stability. However, compared with the MoO\(_2\)-HDA-3 in three-electrode system, the cycle stability of the assembled MoO\(_2\)-HDA-3//MnO\(_2\) device shows a significant decrease. To explore the causes, we tested the cycle stability of the MnO\(_2\) anode. The results showed that the capacitance loss of the MnO\(_2\) anode could reach 13.4% after 30 000 cycles (Figure S16, Supporting Information), which proved that the decline of the cycle stability of the assembled MoO\(_2\)-HDA-3//MnO\(_2\) device was mainly restricted by the anode MnO\(_2\).

The design of flexible devices is essential for the commercialization of supercapacitors. Herein, we assembled flexible all-solid-state devices using MoO\(_2\)-HDA-3 as anode, MnO\(_2\) as cathode, and PVA/LiCl as gel electrolyte, respectively. The CV and GCD curves of the designed flexible device are recorded in Figures S17 and S18, Supporting Information. Symmetrical and linear profiles show ideal capacitive behavior, similar to aqueous devices. The specific capacitance of the flexible device can reach 131 F g\(^{-1}\) at 0.3 A g\(^{-1}\), and even when the current density is increased by ten times, there is still 56 F g\(^{-1}\) (Figure 7g).

When cycling durability of flexible devices was tested at 100 mV s\(^{-1}\) (Figure S19, Supporting Information), obviously, the specific capacitance retained 85.1% after 10 000 cycles. Compared with aqueous devices, the cycling durability of flexible devices is significantly attenuated, which can be attributed to the volatilization of the electrolyte in the gel. Furthermore, the electrochemical performance of flexible devices under different deformation conditions (different bending angels and times) was tested. Encouragingly, the electrochemical performance of flexible devices at different bending angles (0°, 30°, 60°, 90°, 120°) is not significantly sacrificed (Figure 7h), and the specific capacitance retention of the flexible device can reach 96.2% after bending at 90° for 100 cycles (Figure 7i), confirming the vast potential for practical applications.

Pouch devices have been used in the field of high-energy batteries due to their higher safety, lighter weight, and more flexible size adjustment. To evaluate the practicability of the assembled asymmetric device (MoO\(_2@\)HDA-3//MnO\(_2\)), a vacuum sealing machine (shown in Figure 8a) is used with MoO\(_2@\)HDA-3//MnO\(_2\) as the cell, aluminum–plastic film as the shell, and Ni–C as the tab-lead to encapsulate the pouch devices (Figure 8b).

The rectangular-like CV curves, presented in Figure 8c, and the triangular GCD curves, displayed in Figure 8d, of the pouch device confirm the typical capacitive behavior and fast ionic/electron transmission. As expected, the encapsulated pouch device also delivered an excellent specific capacitance of 74.7 F g\(^{-1}\) at 0.2 A g\(^{-1}\) (Figure 8e), and the further energy density is shown in Figure 8f. More realistic energy density of the pouch device (41.5 Wh kg\(^{-1}\)) surpasses commercial batteries such as Ni-Fe batteries (≈20–40 Wh kg\(^{-1}\)), V-based redox flow batteries (≈10–20 Wh kg\(^{-1}\)), and Pd-acid batteries (≈30–40 Wh kg\(^{-1}\)) (Table S6, Supporting Information), demonstrating the feasibility of the three-in-one strategy for the design of high-energy supercapacitors. Compared with aqueous devices, the electrochemical performance of pouch devices has decreased, which can be explained by three aspects. First, the reduction of the electrolyte ratio in the encapsulated device leads to a longer Li\(^+\) transfer path, which increases the internal resistance of the device and further aggravates the heat loss during operation. Then, the permeation path of the electrolyte to the electrode is mainly carried out from the separator along the electrode thickness direction, which makes it more difficult for the electrode material close to the current collector to be fully penetrated by the electrolyte. Finally, the electrolyte will decompose to generate gas during the operation of the pouch device, resulting in the expansion of the internal space, which can cause a local short circuit. Synergistic effects lead to degradation of electrochemical performance of encapsulated pouch devices.

The encapsulated device is inevitably subject to external stimuli such as pressure, impact, and high temperature during actual operation. For this reason, we tested the stability of the pouch device under a variety of extreme conditions. First, the pressure resistance of the pouch device was tested. It is worth noting that under the pressure of different counterweights (10, 20, 50, and 200 g), the shape of the CV curves of the pouch device does not change significantly, indicating good pressure resistance (Figure 8g). Immediately afterward, we tested the effects of high temperature and heavy strikes on working pouch devices (Video S1, Supporting Information). In order to better verify the high temperature resistance of the device, we tested the specific capacitance of the device under different firing times and temperatures. Figure S20, Supporting Information, confirms that the device retains 97% of the initial specific capacitance after the lighter flame continues to burn for 20 s, indicating that our pouch device can effectively resist short-term open flame heating. In addition, the specific capacitance of pouch device continues to rise as the operating temperature increases (Figure S21, Supporting Information), which is better than most of the recently reported representative devices.

While discussing the performance of pouch devices, we concluded that the key to improving the lifetime of pouch devices is the optimization of the design of the pouch device. In particular, the design of the electrolyte plays an important role in improving the performance of pouch devices. For example, the electrolyte should have a high heat stability, low volatility, and fast ionic/electron transmission. In addition, the electrolyte should have a high ionic/electron transmission to ensure the fast charge and discharge of pouch devices. Finally, the electrolyte should also have a long-term stability, which can be achieved through the optimization of the electrolyte composition.
Figure 8. a) Optical photo of secondary packaging machine. b) Schematic diagram of the encapsulating process of pouch device. c) CV curves of the pouch device tested in different scan rate. d) GCD curves of pouch device measured at 0.2–1 A g\(^{-1}\). e) Specific capacitance of pouch device measured at various current densities. f) Ragone plots of pouch device; the inset shows the encapsulating structure. g) CV curves of pouch device under different counterweights at 10 mV s\(^{-1}\). h) CV curves of the four series pouch device tested in different scan rate. i) GCD curves of the four series pouch device tested in various current densities. j) Series connected pouch device run tablets and smartphones.
operation of 3C products usually requires a higher voltage, so we connected four sets of pouch devices in series, and further tested the CV curves (Figure 8h) and GCD curves (Figure 8i) at 0–8 V. As expected, compared with a single pouch device, the CV curves and GCD curves of the series pouch devices also maintain a regular rectangle and a symmetrical triangle. It is commendable that our encapsulated pouch devices can be used as stand-by power source for 3C products (Figure 8j and Videos S2 and S3, Supporting Information), confirming the vast potential for commercialization.

3. Conclusions

In this work, we successfully synthesized three-in-one alkylamine-tuned MoO$_3$ with expanded interlayer spacing, abundant oxygen vacancies, and conductive flexible graphite carbon through simple alkylamine intercalation and carbonization strategies. The enlarged interlayer spacing can not only provide more abundant redox sites, but also ensure a faster ion and electron transmission path. The introduction of oxygen vacancies can also increase the conductivity while promoting the adsorption and diffusion of Li$^+$ in MoO$_3$. Besides that, the flexible graphitic carbon between the MoO$_3$ layers can effectively alleviate the volumetric expansion during the electrochemical charge/discharge process to enhance the long-cycle stability. Compared with pure MoO$_3$, the energy storage capacity of the modified MoO$_3$ has been greatly enhanced due to the abovementioned synergistic effect. With optimized premises, the prepared MoO$_3$-HDA-3 electrode delivered incredible specific capacitance (717 F g$^{-1}$ at 1 A g$^{-1}$), excellent rate capability (specific capacitance retention of 71.5% at 10 A g$^{-1}$), and ultralong cycle durability (no obvious specific capacitive loss after 100 000 cycles). Meanwhile, the assembled MoO$_3$-HDA-3/MnO$_2$ device can operate stably with a high voltage window of 2 V, and shows an exceptional energy density of 78.2 Wh kg$^{-1}$ at the power density of 300 W kg$^{-1}$. More significantly, the encapsulated aqueous pouch devices can be connected in series to run a variety of electronic products (electric fans, tablets, smartphones, etc.), while it can resist strong external interference. Our research demonstrates that the advanced three-in-one strategy is essential for the improvement of the electrochemical performance of metal oxides, which is of practical significance for the commercial applications.

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.

Data Availability Statement

Research data are not shared.

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