Amorphization boost multi-ion storage for high-performance aqueous batteries

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Abstract

Regarding the complex properties of various cations, the design of aqueous batteries that can simultaneously store multi-ions with high capacitance and satisfactory rate performance is a great challenge. Here we report an amorphization strategy to boost cation-ion storage capacitances of anode materials. Consequently, amorphous MoO$_x$ achieves high capacitance in variety of monovalent (H$^+$, Li$^+$, K$^+$), divalent (Mg$^{2+}$, Ca$^{2+}$, Zn$^{2+}$) and even trivalent (Al$^{3+}$) aqueous electrolyte, which is more than 4 times higher than that of crystalline MoO$_x$, and exceeds other reported multiple-ion storage materials. Both experiment and theory calculations reveal ample of active site and isotropic ion are generated in amorphous phase, accelerating cation migration within the bulk of electrode. By coupling with multi-ion storage cathodes, the assembled electrochemical energy storage devices with different carriers display promising energy density and high power density (>15000 W kg$^{-1}$), demonstrative of great potential as advanced aqueous batteries.

Introduction

Electrochemical energy storage devices with high security, long service life, and high energy/power density are urgently desired in modern society.$^1$ Lithium ion batteries occupy a predominant market share owing to their relatively high energy densities. However, the safety problem associated with flammable organic electrolytes and the limited terrestrial reservation of lithium have hindered the implementation of lithium ion batteries in high-demand large-scale equipment. Aqueous rechargeable batteries using abundant multi-ion cations, such as Na$^+$, K$^+$, Ca$^{2+}$, and Mg$^{2+}$ are promising alternatives in the energy storage field.$^2$–$^4$ Water-based electrolytes are intrinsically safe as the nonflammable and nontoxic solvate.$^5$–$^8$ Moreover, the rich abundance and low cost of cations offer better opportunities for large-scale applications.$^9$–$^{10}$ To explore promising aqueous rechargeable batteries with multiple cations, advanced materials allowing fast and reversible ions intercalation is highly desired, which is important for high electrochemical performance of the batteries.

Despite continuous progress, only a few layered materials (e.g., MXene,$^{11}$ MoS$_2$,$^{12}$,$^{13}$ and activated layered double hydroxides$^{14}$,$^{15}$) have been successfully explored for reversible multiple-cation intercalation. One of the main reasons is the complex properties of various cations (e.g., Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Zn$^{2+}$, and Al$^{3+}$): some cations can be stored only at specific active sites, which may be unavailable in the embedded crystallographic planes.$^{16}$ For example, H$^+$, Li$^+$, and Na$^+$ insert into the (001) planes of V$_2$O$_5$, whereas Al$^{3+}$ intercalation into that plane is inhibited by large electrostatic forces.$^{17}$ Limited ion channels and electrostatic repulsion in crystalline materials further hinder the intercalation/deintercalation of guest ions.$^{18}$ Especially, repeated intercalation and deintercalation in the rigid open framework of a crystal causes serious structural distortion, leading to fast capacitance decay. The amorphization of crystalline materials can in principle boost the multi-ion storage capabilities.$^{18}$–$^{20}$ The random long-range networks in the amorphous phase provide ample isotropic ion diffusion routes.
and large numbers of active sites (defects/vacancies) that enhance the ion-intercalation pseudocapacitance of the material.\textsuperscript{16} Furthermore, the loose structure of amorphous materials usually accommodates small lattice distortion and volume expansion during cation insertion/extraction, which enhances the cycling stability.\textsuperscript{19,21} Unfortunately, to our knowledge, amorphization engineering for multi-ion storage has not been reported.

Herein, we develop an amorphization strategy to boost the cation-ion storage capacitances of anode materials. As a demonstration, we select amorphous MoO\textsubscript{x} (A-MoO\textsubscript{x}), which possesses a disordered atomic arrangement with a controllable multi-valance Mo redox center for cation accommodation. Amorphization largely enhances the energy storage performance of MoO\textsubscript{x} in electrolytes of various metal/non-metal cations. More specifically, the capacitances in H\textsuperscript{+}, Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Zn\textsuperscript{2+}, and Al\textsuperscript{3+} electrolytes reached 830, 466, 512, 328, 541, 570, 717, and 886 F g\textsuperscript{−1}, respectively, exceeding those of crystalline MoO\textsubscript{x} (by more than fourfold) and other multiple-ion storage materials reported in the recent literature. Experimental analysis and theoretical calculations confirm that A-MoO\textsubscript{x} provides more exposed active sites and ion channels than crystalline MoO\textsubscript{x}, accelerating charge-transfer and ion diffusion and hence improving the energy storage performances. All-aqueous batteries formed by coupling A-MoO\textsubscript{x} with an electrochemically activated layered double hydroxides cathode achieved high energy density, high power density, and long cycle life with different cations, demonstrating the great potential of A-MoO\textsubscript{x} in safe future power supplies.

\textbf{Fabrication And Characterization Of A-moox}

The uniform amorphous MoO\textsubscript{x} (A-MoO\textsubscript{x}) layer with a thickness of \textasciitilde 2.5 \(\mu\text{m}\) was successfully grown on Mo substrate by an anodization strategy (details see Supporting Information), as confirmed in scanning electron microscopy and atomic force microscopy observations (Fig. 1a). The anisotropic amorphous structure of A-MoO\textsubscript{x} was further revealed by the absence of lattice fringes in the transmission electron microscopy (HRTEM) image (Fig. 1b) and the diffuse halo ring in the corresponding selected area electron diffraction pattern. The X-ray diffraction patterns of A-MoO\textsubscript{x} (Fig. 1c) show no identifiable diffraction peaks of Mo oxides, which is consistent with the HRTEM image. The amorphous nature was maintained at temperatures up to 400°C. The amorphous phase was largely transformed to the monoclinic (\textit{P2}_{1}/\textit{n}) MoO\textsubscript{2} phase \textit{in situ} (hereafter denoted as C-MoO\textsubscript{x}), at temperatures of 500°C and higher. The survey spectrum obtained by X-ray photoelectron spectroscopy (XPS) verified the presence of Mo, O and C elements in A-MoO\textsubscript{x} (Supplementary Fig. 1). The composition and morphology remained almost unchanged after the crystallization process (Supplementary Fig. 2 and Supplementary Fig. 3). Three doublets in the high-resolution Mo 3d XPS spectrum of A-MoO\textsubscript{x} were ascribed to the Mo 3d\textsubscript{5/2} and Mo 3d\textsubscript{3/2} orbitals of Mo\textsuperscript{6+}, Mo\textsuperscript{5+} and Mo\textsuperscript{4+}, suggesting multi-oxide species of Mo. The Raman spectrum of A-MoO\textsubscript{x} shows several peaks at 100–1000 cm\textsuperscript{−1} corresponding to in-plane and bending vibration modes of Mo-O (Supplementary Fig. 4). However, the intensities of the Mo–O stretching vibrations are lower in A-MoO\textsubscript{x} than in C-MoO\textsubscript{x}, revealing weak interactions of the Mo-O bonds in A-MoO\textsubscript{x}.
The localized coordination environments of the Mo sites in A-MoO\textsubscript{x} and C-MoO\textsubscript{x} are further derived from X-ray absorption near-edge spectra (XANES) measurements. The slightly positively shifted rising edge around 20005 eV in the XANES spectrum of A-MoO\textsubscript{x} suggests that electron density decreases around the Mo sites (Supplementary Fig. 5). The lower amplitudes of the corresponding Mo K-edge k3\(\chi\)(k) oscillation curves in A-MoO\textsubscript{x} than in C-MoO\textsubscript{x} indicate a variable coordination environment of Mo (Fig. 1d). In addition, the bonding and coordination changes in A-MoO\textsubscript{x} and C-MoO\textsubscript{x} were elucidated by extended X-ray absorption fine structure spectroscopy (see Fig. 1e and the summary in Table S1). The greater Debye–Waller factor of A-MoO\textsubscript{x} than of C-MoO\textsubscript{x} reveals a more disordered structure around the molybdenum atom in A-MoO\textsubscript{x}. Consequently, the bond distances of the dominant Mo—O\textsubscript{1} and Mo—O\textsubscript{2} coordination are longer in A-MoO\textsubscript{x} (2.15 and 2.03 Å, respectively) than in crystalline C-MoO\textsubscript{x} (2.04 and 1.92 Å, respectively). More strikingly, the coordination numbers of Mo—O\textsubscript{1} and Mo—O\textsubscript{2} in A-MoO\textsubscript{x} (1.4 and 1.4, respectively) deviated significantly from those in C-MoO\textsubscript{x} (2.3 and 1.2, respectively), suggesting that molybdenum vacancies formed in A-MoO\textsubscript{x}. As these vacancies distorted the Mo octahedrons, unpaired electrons were detected in the electron paramagnetic resonance (EPR) spectroscopy results of A-MoO\textsubscript{x} (Supplementary Fig. 6). In the EPR spectrum of A-MoO\textsubscript{x}, the peak centered at ~364.5 mT with a corresponding g-value of 1.924 is attributed to unpaired electrons on the Mo 3d\textit{xy} orbital, whereas the g-values of 1.969 and 1.903 are attributed to single-electron signals on the Mo 3d\textit{xz} and 3d\textit{yz} orbital, respectively. This result suggests a higher proportion of unsaturated Mo in the amorphous than in the crystalline structure, indicating the existence of molybdenum vacancies in both the surface and bulk of the electrode.\textsuperscript{22–24} These vacancies provide active sites for ion embedding. Furthermore, the variable atom-coordination environment of A-MoO\textsubscript{x} is amenable to the formation of open channels and an unrestricted structure that accelerates ion diffusion within the solid state (Fig. 1f).

**Electrochemical Performance Of Moox**

The electrochemical performances of MoO\textsubscript{x} with different crystallites are first investigated with a three-electrode configuration in 0.5 mol L\textsuperscript{−1} Na\textsubscript{2}SO\textsubscript{4} aqueous solution. The cyclic voltammetry (CV) curves of A-MoO\textsubscript{x} show the characteristic shape of a pseudocapacitive response (rectangular with wide peaks).\textsuperscript{25} When the post-annealing temperature increased to 500°C, the redox pairs disappears (Fig. 2a), indicating an electric double-layer capacitance created by hard intercalation of ions into the C-MoO\textsubscript{x} lattice. From the CV curves, the capacitance of A-MoO\textsubscript{x} is determined as 512 F g\textsuperscript{−1} (819 F cm\textsuperscript{−3}) at 2 mV s\textsuperscript{−1}, 4.5 times higher than that of C-MoO\textsubscript{x} (Fig. 2b). It should be noted that the Mo substrate negligibly contributed to the capacitance (Supplementary Fig. 7). Despite surface area different may attribute to both electrochemical double layer capacitance (EDLC)information, \textit{i.e.}, the capacitance increasing is more likely attribute to the atomic arrangement. Moreover, the rectangular shape of the CV curves is maintained at scan rates up to 100 mV s\textsuperscript{−1} and the capacitance remained high (~50%) (Fig. 2b and Supplementary Fig. 8), indicating the excellent rate performance of A-MoO\textsubscript{x}. This result is consistent with the galvanostatic charge-discharge (GCD) curves, in which the potential linearly varied with discharge time at various charging
rates (Supplementary Fig. 9). To meet the requirements of practical applications, we fabricated A-MoO\textsubscript{x} with various mass loadings on Mo mesh (Supplementary Fig. 10). The high specific capacitance of A-MoO\textsubscript{x} is maintained even under a mass loading of 8.1 mg cm\textsuperscript{−2}, suggesting the favorable intercalation pseudocapacitive behavior. Furthermore, the amorphous structure endows A-MoO\textsubscript{x} with outstandingly stable cycling performance, \textit{i.e.}, high capacitance retention 94.5\% after 20000 cycles (Fig. 2c). Moreover, the practical electrodes (\textit{e.g.}, A-MoO\textsubscript{x} powder mix with binder and carbon black) also exhibits high capacitance retention of 92.3\% in 10000 cycles (Supplementary Fig. 11). The present study evaluates whether the high storage properties of MoO\textsubscript{x} are expandable to other monovalent (H\textsuperscript{+}, Li\textsuperscript{+}, K\textsuperscript{+}), divalent (Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Zn\textsuperscript{2+}) and trivalent (Al\textsuperscript{3+}) aqueous carrier candidates with different physicochemical properties. Figure 2d and Supplementary Fig. 12 compare the CV curves of A-MoO\textsubscript{x} and C-MoO\textsubscript{x} in various aqueous solutions containing the above cations. The monovalent carriers yielded quasi-rectangular curves with large integrating areas under broad redox peaks at a low scan rate (5 mV s\textsuperscript{−1}), indicating a pseudocapacitive behavior of their intercalation process. The divalent (Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Zn\textsuperscript{2+}) and trivalent (Al\textsuperscript{3+}) aqueous carriers with larger electrostatic forces also delivered favorable electrochemical performance. In contrast, the CV curves of C-MoO\textsubscript{x} gives small integrating areas in all of the above-mentioned aqueous solutions. Figure 2e summarizes the energy storage capacitance changes during the crystallization process of MoO\textsubscript{x} in various cation-based electrolytes. High capacitance of 830, 466, 512, 328, 541, 570, 717 and 886 F g\textsuperscript{−1} are obtained in the H\textsuperscript{+}, Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Zn\textsuperscript{2+} and Al\textsuperscript{3+} summarizes the energy storage capacitance changes during the crystallization process of MoO\textsubscript{x} in various cation-based electrolytes, electrolytes, respectively. It is worth noting that cation species are most richly accommodated in the metal oxides. Moreover, the above capacitances significantly exceeded that of C-MoO\textsubscript{x} (in which the capacitance is only 25\% that of A-MoO\textsubscript{x}) and those of other multiple-ion storage materials reported in the recent literature (Fig. 2f).\textsuperscript{11–14,26–31} Besides, the capacitance of other type materials (\textit{e.g.} TiO\textsubscript{2}) can also be improved by amorphization engineering (Supplementary Fig. 13).

The multi-cation (de-)intercalation mechanism of A-MoO\textsubscript{x} is determined by analyzing the electrochemical dynamics of carrier-doped A-MoO\textsubscript{x}. The capacitive-capacitance contribution to the total capacitance is quantified as \textit{i} = \textit{a v} + \textit{b v}^{0.5}, where \textit{a v} and \textit{b v}^{0.5} describe the pseudocapacitive-controlled behavior and diffusion-limit process, respectively. The pseudocapacitance of A-MoO\textsubscript{x} accounted for 57\% of the total capacitance at 2 mV s\textsuperscript{−1} and gradually increased with scan rate, reaching 91\% at 100 mV s\textsuperscript{−1} (Fig. 3a,b). The high proportion of desirable pseudocapacitive behavior indicates fast ion diffusion among the disordered atoms of the amorphous solid state. The pseudocapacitive intercalation process was further investigated via multiple-step chronoamperometry (MUSCA, Supplementary Fig. 14, see Methods for details)\textsuperscript{32} The reconstructed CVs of A-MoO\textsubscript{x} exhibits a rectangular shape with identifiable peaks (Fig. 3c). Applying the formula \textit{log(i)} = \textit{a} + \textit{b log(υ)} to the cathodic and anodic current densities of A-MoO\textsubscript{x}, the \textit{b}-values are determined as 0.72–0.86 and 0.72–0.97, respectively (Fig. 3d). As \textit{b} = 0.5 and \textit{b} = 1.0 correspond to diffusion-controlled and pseudocapacitive processes, respectively\textsuperscript{33} these findings further confirm the dominance of pseudocapacitive behaviors. The diffusion barrier within solid state A-MoO\textsubscript{x}
was calculated using the galvanostatic intermittent titration technique (Supplementary Fig. 15). In the discharge state, the average diffusion coefficient \( D \) ranged from \( 5 \times 10^{-9} \) to \( 5 \times 10^{-10} \) \( \text{cm}^2 \text{ s}^{-1} \) (Fig. 3e), higher than those of \( \text{Na}^+ \)-assisted energy storage in battery/supercapacitor systems.\(^{34}\) The high \( D \) indicates the fast immigration of cations through amorphous A-MoO\(_x\). The Nyquist plots of MoO\(_x\) show semicircular arcs in the high-frequency range and nearly straight branches in the low-frequency region (Fig. 3f) corresponding to charge-transfer resistance \( (R_{ct}) \) and diffusion resistance (Warburg impedance \( Z_w \)) within the solid state, respectively. The \( R_{ct} \) values gradually decreases with increasing atomic ordering, being two orders of magnitude smaller in A-MoO\(_x\) (70 \( \Omega \) \( \text{cm}^2 \)) than in C-MoO\(_x\) (\( \sim 1600 \Omega \) \( \text{cm}^2 \)) in \( \text{Na}^+ \) solution. The intercalation kinetics of MoO\(_x\), represented by the activation energies \( E_a \), were derived from the \( R_{ct} \) using the Arrhenius equation (Fig. 3g and Supplementary Fig. 16).\(^{35}\) A-MoO\(_x\) shows a much lower \( E_a \) than C-MoO\(_x\) (27.3 kJ mol\(^{-1}\) versus 40 kJ mol\(^{-1}\)), suggesting faster charge-transfer kinetics through the amorphous structure. The fast charge-transformation and diffusion process of \( \text{Na}^+ \) in A-MoO\(_x\) was successfully extended to the other typical monovalent, divalent and trivalent cations (Supplementary Fig. 17 and Supplementary Fig. 18, Tables S2 and S3).

The electron transfer and ion transport properties of the MoO\(_x\) electrodes during the charging/discharging process were obtained through staircase potentiodynamic electrochemical impedance spectroscopy (Supplementary Fig. 19). Figure 3h presents 3D Bode-style “waterfall” plots of A-MoO\(_x\) and C-MoO\(_x\), which relate the calculated capacitance \( (C) \), frequency, and potential (see Methods for details). The \( C' \) of A-MoO\(_x\) gradually increases with decreasing frequency and was maximized in the low-frequency region (< 1 Hz). This characteristic pseudocapacitive behavior is observed in all potential ranges. Meanwhile, C-MoO\(_x\) yields small \( C' \) values with gentle roll-off at low frequencies, indicating that cation intercalation lowly contributed to the total capacitance. The 3D plots of normalized capacitance \( (C'') \) further confirmed the sluggish intercalation process of C-MoO\(_x\) and the high relaxation time constant \( (\tau > 10 \text{ s}) \) proves the electric double-layer capacitive nature of this material (Supplementary Fig. 20).\(^{36}\) In contrast, the \( \tau \) of A-MoO\(_x\) is around 1.0 s across the potential range \(-1\) to 0 V, revealing fast and reversible cation intercalation pseudocapacitive processes in the amorphous phase.

Figure 3i shows the \textit{in situ} Raman spectra of A-MoO\(_x\) during the charging/discharging process. The stable peak of \( \nu_x\text{SO}_4^{2-} \) (450 cm\(^{-1}\)) in \( \text{Na}_2\text{SO}_4 \) electrolyte is assigned to adsorbed \( \text{SO}_4^{2-} \) on the A-MoO\(_x\) electrode or near surface zone.\(^{37}\) No new peaks appear in the 3D contour plot during the charging process (0 V to \(-1\) V), but a peak at 260 cm\(^{-1}\) emerges during the discharging process, which is assigned to vibrations of cations and \( \text{SO}_4^{2-} \) (M–OSO\(_3\)).\(^{37}\) It is inferred that \( \text{Na}^+ \) deintercalated from the A-MoO\(_x\) bulk and forms weak chemical bonds with the adsorbed \( \text{SO}_4^{2-} \) or \( \text{SO}_4^{2-} \) in near surface zone. The intensity of the M-OSO\(_3\) signal progressively decreases and finally disappears during the discharging process, demonstrating that \( \text{Na}^+ \) intercalation/deintercalation is reversible within the A-MoO\(_x\) electrode. In contrast, C-MoO\(_x\) produces a negligible Na-OSO\(_3\) signal in in-situ Raman (Supplementary Fig. 21), confirming that
Na\(^+\) is hardly intercalated in the C-MoO\(_x\) lattice; that is, the energy storage mechanism in C-MoO\(_x\) is double-layer capacitance. Note that Na\(^+\) intercalation into A-MoO\(_x\) may be accompanied by a small degree of proton insertion because H\(^+\) is ubiquitously present at low concentrations in water, as reflected by the reversible pH changes (from 7.08 to 7.14 and back to 7.08) in operando pH measurements (Supplementary Fig. 22). The active charge carriers and the topochemistry mechanism is also investigated by operando electrochemical quartz crystal microbalance measurements. Supplementary Fig. 23 shows the A-MoO\(_x\) experiences a mass increasing at a rate of 16 g/mol e\(^-\), which suggests that the charging process involves Na\(^+\) (23 g/mol e\(^-\)) and H\(^+\) (1 g/mol e\(^-\)) co-intercalation mechanism. The Na\(^+\) releases quickly from bulk during the extraction of charge, which is likely to combine with SO\(_4^{2-}\) and detected by Raman spectrum. During repeated charging and discharging, the A-MoO\(_x\) retains its nanoporous morphology and amorphous structure (Supplementary Fig. 24), which is deviated from the high-performance amorphous Nb\(_2\)O\(_5\) reported in the recent literature.\(^{38}\) Moreover, the postmortem SEM shows no structural changes after cycling (shown in Supplementary Fig. 24).

Density functional theory (DFT) calculations are employed to further investigate the intercalation process in A-MoO\(_x\) and C-MoO\(_x\). The structural models of MoO\(_x\) counterparts (amorphous and crystalline) based on XANES results are shown in Fig. 4a and Supplementary Fig. 25 for comparison. The Na\(^+\) diffusion route in the material bulk and the corresponding energy profiles are shown in Fig. 4b. The loose structure of the amorphous phase and longer Mo-O bonds effectively reduce the space resistance for Na\(^+\) migration and thus lower the energy barrier. The energy barrier of sodium-ion transport through A-MoO\(_x\) is as low as 0.6 eV, suggesting the feasibility of Na\(^+\) diffusion through the structure on the unique amorphous isotropic ion diffusion routes. In contrast, the high repulsive interaction between Na\(^+\) and the crystalline skeleton raises the diffusion barrier of C-MoO\(_x\) to above 1 eV. The disordered structure also attributed to increasing adsorption energy (\(E_{ad}\)) on the electrode surface. Figure 4c displays the DFT-calculates charge-density differences. The results confirm strong electrostatic interactions and polarization in A-MoO\(_x\), which improves the adsorption ability and increases the speed of Na-storage kinetics in the amorphous structure. Moreover, the other cations (e.g., H\(^+\), Li\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Zn\(^{2+}\), Al\(^{3+}\)) also exhibit high \(E_{ad}\) with amorphous A-MoO\(_x\), indicating the favorable intercalation process of A-MoO\(_x\). More interestingly, the \(E_{ad}\) toward different cation are high relative to the capacitance of A-MoO\(_x\), e.g., \(E_{ad}\) of H\(^+\) > Al\(^{3+}\) > Zn\(^{2+}\) > Ca\(^{2+}\) > Mg\(^{2+}\) > Na\(^+\) > Li\(^+\) > K\(^+\) (Fig. 4d and Supplementary Fig. 26).

The potential applications of A-MoO\(_x\) are assessed in multiple-ion aqueous batteries with different cation carriers. Electrochemically activated CoNi layered double hydroxide developed by our group\(^{14}\) and a Prussian blue analog were selected as the cathode pairs to the A-MoO\(_x\) anode because they possess high potential and high capacitance for various cations (Fig. 5a and Supplementary Fig. 27). As expected, the assembled batteries exhibit favorable energy storage performances in all cation-based electrolytes. The CV profiles of the A-MoO\(_x\)-based batteries with different electrolytes are nearly rectangular with large integrated areas and several broad redox peaks, indicating a pseudocapacitive response (Fig. 5b). The
GCD curves of the assembled battery with Na\(^+\) at various current densities (0.2 to 10 A g\(^{-1}\)) is symmetric with a long discharge time (Fig. 5c).

In the cell with a current density of 0.2 A g\(^{-1}\), the specific capacitance reaches 165 F g\(^{-1}\) (Fig. 5d). The fabricated batteries with monovalent, divalent, and trivalent ion electrolytes also achieve high capacitances (e.g., 280 F g\(^{-1}\) in Zn\(^{2+}\), 251 F g\(^{-1}\) in Al\(^{3+}\); Fig. 5e). Benefiting from the high capacitance and large voltage window, all batteries deliveres higher energy density (e.g., 82 Wh kg\(^{-1}\) in Na\(^+\), 130 Wh kg\(^{-1}\) in Zn\(^{2+}\) at 150 W kg\(^{-1}\)) and power density (~15000 W kg\(^{-1}\)) than the reported asymmetric supercapacitors and their performances are comparable to those of commercial Li-ion batteries.\(^{39,40}\) The assembled batteries also exhibits superior stability at a current density of 10 A g\(^{-1}\) (Fig. 5f), demonstrating their promising application in long-term storage systems. To verify the viability of the batteries as power sources, an individual pouch cell (2 cm × 4 cm) was fabricated with high energy density of 42 Wh kg\(^{-1}\) (Supplementary Fig. 28). The light-emitting diode arrays are brightened two cells in series connection after 10 s of charging time (Fig. 5g, Mov. S1). Such a short charging time is highly desired in electric vehicles, portable electronics, and energy storage systems with high power density requirements.

**Conclusion**

In summary, amorphous materials with disordered atomic arrangements and increased atomic spacing provide ample numbers of active sites and isotropic ion diffusion routes for various cations. As a typical example, A-MoO\(_x\) exhibits enhanced energy storage performance while hosting various cations, yielding capacitances of 830, 466, 512, 328, 541, 570, 717 and 886 F g\(^{-1}\) in H\(^+\), Li\(^+\), Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Zn\(^{2+}\) and Al\(^{3+}\) solutions, respectively. Both the performance and variety of accommodate cation species exceeded those of other multiple-ion storage materials reported in the recent literature. Experimental and theoretical calculations support the fast immigration of cations within the amorphous MoO\(_x\) solid state. Aqueous batteries constructed by coupling A-MoO\(_x\) with multi-ion storage cathodes achieves high capacitance in various electrolytes and demonstrate great application potential in safe, low cost, high power-high-density devices.

**Methods**

**Preparation of MoO\(_x\) anode:** Amorphous molybdenum oxides (A-MoO\(_x\)) were prepared by anodization. Briefly, 0.1 mm thick Mo foils were immersed in ethanol and distilled water with ultrasonication for 10 minutes each. The foils were successively dried in air at 60 °C. Anodization was performed in a two-electrode electrochemical cell, where Mo foil was used as anode and a platinum electrode was used as a counter. A-MoO\(_x\) were grown in aqueous electrolyte (containing of 0.4 mol L\(^{-1}\) H\(_3\)PO\(_4\) and 0.01 mol L\(^{-1}\) NH\(_4\)F) at 0.8 V in 2 h. After anodization, the sample was immersed in ethanol to remove residue and dry
at air flow. Reference C-MoO$_x$ were prepared by annealing A-MoO$_x$ were annealed at 200–500°C in N$_2$ for 2 h to transform the amorphous to a crystalline structure.

**Preparation of electrochemical activated layer double hydroxide (ECA-LDH) cathode**: The ECA-LDH was synthesized on carbon cloth via a simple electrosynthesis method and activation process. Before synthesis, carbon cloth was immersed in concentrated nitric acid, ethanol, and deionized water (each for 10 min) to improve hydrophilicity and remove impurities. Then, the electrosynthesis process was operated in an electrochemical cell with a three-electrode, where hydrophilic carbon cloth, Pt plate and Ag/AgCl work as working electrode, counter and the reference electrode. The LDH was grown on carbon cloth in 50 mL aqueous solution (containing 0.15 mol L$^{-1}$ CoCl$_2$ 6H$_2$O and 0.15 mol L$^{-1}$ Ni(NO$_3$)$_2$ 6H$_2$O) at a potential of $-1.0$ V vs. Ag/AgCl. Finally, ECA-LDH was converted by LDH via cyclic voltammetry process in 1 mol L$^{-1}$ KOH with scanning rate of 100 mV s$^{-1}$ at potential window of 0–0.8 V.

**Preparation of prussian blue analogue (PBA) cathode**: The PBA was prepared according to the literature. Typically, 40 ml CuSO$_4$ (0.2 mol L$^{-1}$) was added dropwise into 40 ml of K$_3$Fe(CN)$_6$ solution (0.1 mol L$^{-1}$) under magnetic stirring. After 6 h, the suspension was rinsed with deionized water and centrifuged 3 times, and then dried in air at 60°C. The PBA cathode were prepared using the slurry coating method. PBA were mixed with 10 wt % carbon black and 10 wt % polyvinylidene fluoride (PVDF) in 1-methyl-2-pyrrolidinone (NMP) solvent to form a viscous paste, then cast onto carbon paper. After dry in an oven at 60°C, the active mass loading of 1 mg cm$^{-2}$ PBAs cathode is prepared.

**Characterization**: The morphology investigation was using a Zeiss SUPRA 55 scanning electron microscopes (SEM, with an accelerating voltage of 20 kV), which combine with energy dispersive X-ray spectroscopy (EDX). Transmission electron microscope (TEM) images were recorded using a Philips Tecnai 20 and JEOL JEM-2010 high-resolution transmission electron microscope with an accelerating voltage of 200 kV. Shimadzu XRD-6000 diffractometer with a Cu K$_\alpha$ source was used to measure the X-ray diffraction patterns of the samples (scan range: 5°–80°, scan step: 10° min$^{-1}$). Raman micro spectrometer (Renishaw, in Via-Reflex, 532 nm) was used to carry out the Raman measurements by using a confocal. Thermo VG ESCALAB 250 X-ray photoelectron spectrometer was used to perform the X-ray photoelectron spectra (XPS) of the samples with a pressure of about 2×10$^{-9}$ Pa and using Al K$_\alpha$ X-rays as the excitation source. Electron paramagnetic resonance (EPR) spectra were collected on spectrometer (Bruker ENX-500) with 9.53 GHz X-band at room temperature to investigate oxygen vacancies in A-MoO$_x$. The Co XAFS measurements were performed at the beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS). The typical energy of the storage ring was 2.5 GeV with a maximum current of 250 mA and the hard X-ray was monochromatized with Si (111) double-crystals. Extended X-ray absorption fine structure spectra (EXAFS) were recorded at ambient temperature in fluorescence mode and transformed without phase correction.

**Electrochemical measurements**: Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) analyses were conducted using a CHI660e
electrochemical workstation at room temperature. In any case a three-electrode electrochemical cell was used. The Mo-oxides layers were used as working electrodes; they were pressed against an O-ring-sealed opening in the wall of the electrochemical cell. A graphite electrode was used as a counter. As reference electrode, an Ag/AgCl (3 M KCl) electrode was used. H\(^{+}\), Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), Ca\(^{2+}\), Zn\(^{2+}\) and Al\(^{3+}\) based aqueous solution with the cation concentration of 1 mol L\(^{-1}\) was used as electrolyte.

**Multiple potential step chronoamperometry (MUSCA):** MUSCA tests are intended to minimize ohmic drop contribution in CV plots, thus reflect “true” kinetic study of pseudocapacitive performance of the electrode. The MUSCA of A-MoO\(_x\) carried out by using potential step of -100 mV with a fixed step duration of 120 s from 0 V to -1 V vs Ag/AgCl. Afterward, similar process with a step size of +100 mV was applied to scan the anodic potential range back to 0 V vs Ag/AgCl.

The corrected current via MUSCA at each potential step is given according to:

$$i = \int_{0}^{\Delta t} i \, dt / \Delta t$$

where \(\Delta t\) is the selected time, and \(i\) is the response current.

**Staircase potenti-electrochemical impedance spectroscopy (SPEIS)**

The staircase potenti-electrochemical impedance spectroscopy measurements were performed using an AC amplitude of 5 mV ranging within a frequency range from 100 kHz to 10 mHz at -100 mV intervals from 0 V to -1 V. The real and imaginary components of capacitance as a function of angular frequency (\(\omega\)) can be expressed as below:

$$C' (\omega) = - \frac{Z'' (\omega)}{\omega |Z(\omega)|^2}$$

$$C'' (\omega) = \frac{Z' (\omega)}{\omega |Z(\omega)|^2}$$

In 3D Bode plots, SPEIS measurements are focused in the low-frequency range (1 ~ 0.01 Hz), where these electrodes exhibit a primarily pseudocapacitive response.

**Galvanostatic intermittent titration technique (GITT):**

GITT analysis was obtained by a series of galvanostatic discharge pulses of 30 s at 0.64 mA g\(^{-1}\), followed by a 300 s rest. The chemical diffusion coefficient can be calculated at each step, with the following formula:
\[ D = \frac{4}{\pi \tau} \left( \frac{n_m V_m}{S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2 \]

where \( n_m \) is the number of moles (mol); \( V_m \) is the molar volume of the electrode (cm\(^3\)/mol); \( S \) is the electrode/electrolyte contact area (cm\(^2\)); \( \Delta E_s \) is the steady-state voltage change, due to the current pulse and \( \Delta E_t \) is the voltage change during the constant current pulse, eliminating the iR drop.

**In-situ Raman measurements:**

In-situ Raman was collected using a custom three-electrode system cell without quartz window, allowing laser into the cell during cycling. The cell was flooded with 0.5 mol L\(^{-1}\) Na\(_2\)SO\(_4\). A-MoO\(_x\) worked as work electrode, platinum used as counter, and Ag/AgCl as reference. All spectra were collected at a 532 nm laser in the range of 150 ~ 550 cm\(^{-1}\) with the exposure times of 30 seconds to minimize laser damage to the electrode surface. During cycling the spectra collected at specific potential via GCD measurement.

**Operando electrochemical quartz crystal microbalance (EQCM)**

Operando electrochemical quartz crystal microbalance was performed in an EQCM cell. The EQCM experiments carried out at a scan rate of 10 mV s\(^{-1}\) a specially designed electrolytic cell using a standard three-electrode configuration. Working electrode is prepared as follow: Mo (500 nm) is first sputtered on gold-coated quartz crystal electrode, then anodized in anodization electrolyte for 10 minutes to form A-MoO\(_x\) nanoporous on gold-coated quartz crystal. Platinum electrode and an Ag/AgCl electrode were used respectively as the counter electrode and reference electrode.

The mass different during intercalation/deintercalation process of A-MoO\(_x\) on the quartz surface follow the Sauerbrey equation:

\[ \Delta f = -2 f_0^2 \Delta m (\mu \rho)^{-1/2} / A \]

Here, \( \Delta f \) is the frequency change, \( f_0 \) is the resonant frequency of the quartz crystal (7.995 MHz), \( \mu \) is the shear modulus of quartz (2.947×10\(^{11}\) g/cm\cdot s\(^2\)), \( \rho \) is the density of quartz (2.684 g cm\(^{-3}\)), \( A \) is the area of quartz crystal (0.196 cm\(^2\)).

**Estimation of the weight of the active layer.**

The mass of the A-MoO\(_x\) can be calculated by measuring the weight difference of the A-MoO\(_x\) electrode before and after removal of the oxide layer. Briefly, the mass of as formed A-MoO\(_x\) with Mo substrate was measured by a high-resolution balance. After that, the A-MoO\(_x\) were immersed in 1 mol L\(^{-1}\) KOH and ultrasonicated for 2 min. The Mo substrate was cleaned by distilled water and measured again after removing the oxides layers. To reduce the errors, 10 pieces sample was measured together. Overall, the average mass of the A-MoO\(_x\) layers were found to be 0.4 to 8.1 mg cm\(^{-2}\).
Theoretic calculation:

Ab initio molecular dynamics (AIMD) simulation was carried out to study MoO\textsubscript{x} structures, respectively. The defective structural model was built using ab initio MD simulations and the “melt-and-quench” method. The MoO\textsubscript{2} crystal is melted at high temperatures (5000 K) for 3 ps and then quenched it to room temperature with a superfast cooling rate of $2 \times 10^{14}$ K s\textsuperscript{-1} to allow the formation of the defective phase. During geometry optimization, the cut-off energy was set as 450 eV for structures, respectively. The Brillouin zone was sampled by a Monkhorst-Pack (MP) k-point grid of 1×1×1 for geometry optimizations. The PBE-D3 dispersion term was introduced to correct the van der Waals interactions\textsuperscript{[1]}. The conjugated gradient method was applied with a smearing width of 0.15 eV, and the convergence criteria for the energy and force were $10^{-4}$ eV/cell and 0.05 eV/Å, respectively. AIMD simulations were run for 10 ps as equilibration with time steps of 1 fs, performing a constant temperature of 300 K in the Nosé-Hoover isokinetic ensemble.

The absorption energy calculation was employed the Vienna Ab Initio Package (VASP)\textsuperscript{[2, 3]} to perform all the density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE\textsuperscript{[4]} formulation. Projected augmented wave (PAW) potentials\textsuperscript{[5, 6]} was described the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 520 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10 – 4 eV. A geometry optimization was considered convergent when the force change was smaller than 0.05 eV/Å. Grimme’s DFT-D3 methodology\textsuperscript{[7]} was used to describe the dispersion interactions. The Brillouin zone integral uses the surfaces structures of 2×2×1 monkhorst pack K-point sampling. Finally, the adsorption energies($E_{ads}$) were calculated as:

$$E_{ads} = E_{ad/sub} - E_{ad} - E_{sub}$$

where $E_{ad/sub}$, $E_{ad}$, and $E_{sub}$ are the total energies of the optimized adsorbate/substrate system, the adsorbate in the gas phase, and the clean substrate, respectively. The Climbing Image-Nudged Elastic Band methods had been employed to calculate the Na ions migration barriers structures.

Assembly of the energy storage device:

The pouch cell was assembled with two electrodes by using the A-MoO\textsubscript{x} as the anode and ECA-LDH or PBA as the cathode, and fiberglass paper working as separate. 1 mL of electrolyte is injected into the bag followed by a vacuum packaging with a vacuum sealing machine.

Calculation of electrochemical double layer capacitance (EDLC):

The calculation for EDLC based on formula, where $C_s$ equal to ~ 0.035 mF cm\textsuperscript{-2} in H\textsubscript{2}SO\textsubscript{4} solution:

$$C_{EDLC} = C_s * S_{ESCA} (S_{ESCA} < S_{BET})$$
Less than 44 F/g and 2.2 F/g are contributed to the EDLC for A-MoO$_x$ and C-MoO$_x$ respectively, which is only 5% and 2% of total capacitance.

**Declarations**

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**Author contributions**

B.J. and Y.L designed and carried out materials fabrication, characterization, analysis of the results and wrote the manuscript. J.C, S.Z, Y.W, A.X and M.X discussed and regulated the experiments. M.S. supervised the project, conceived the idea, helped design the experiments, analyzed the data and wrote the manuscript. All authors discussed the results and contributed to preparing the manuscript.

**Competing interests**

The authors declare no competing financial interests.

**Additional information**

Supplementary information is available for this paper at https://doi.orgxxxxxx.

**Data availability.** The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

**References**


**Figures**

**Figure 1**

**Structure and morphology of MoO$_x$** a, High magnification SEM image of A-MoO$_x$ (inset: corresponding AFM image of top-view). b, In-situ XRD pattern of MoO$_x$ in crystallization process. c, High magnification TEM image of A-MoO$_x$ (inset: corresponding SAED pattern). d, Mo K-edge extended XANES oscillation functions k$^3$χ(k) of A-MoO$_x$ and C-MoO$_x$. e, Magnitude of k$^3$-weighted Fourier transforms of Mo K-edge EXAFS spectra for A-MoO$_x$ and C-MoO$_x$. f, Schematic of the atomic arrangement changes during crystallization process.
Figure 2

**Electrochemical performance of MoO\textsubscript{x}**  
**a** CV curves of MoO\textsubscript{x} with different post-annealing temperature at a scan rate of 2 mV s\textsuperscript{-1}.  
**b** Gravimetric capacitances of MoO\textsubscript{x} versus scan rate.  
**c** Cycling performance of A-MoO\textsubscript{x} at 10 A g\textsuperscript{-1} for 20-thousands cycles.  
**d** CV curves of A-MoO\textsubscript{x} and C-MoO\textsubscript{x} in various electrolyte.  
Mo K-edge extended XANES oscillation functions k3\chi(k) of A-MoO\textsubscript{x} and C-MoO\textsubscript{x}.  
**e** The relationship between capacitance with crystallite for MoO\textsubscript{x} in various electrolyte.  
**f** Comparison of the capacitance in different electrolyte between this work and references.
Figure 3

**Electrochemical performance of MoO$_x$**

**a**, Calculated capacitive contribution of A-MoO$_x$ at scan rate of 2 mV s$^{-1}$ and 100 mV s$^{-1}$. **b**, Capacitance contribution ratio of A-MoO$_x$ and C-MoO$_x$ at different scan rates. **c**, CVs calculated from MUSCA analysis in 0.5 M Na$_2$SO$_4$ at various scan rate. **d**, Lineal fits obtained for Log (currents density) vs. Log (scan rate) at various potential. **e**, The diffusion coefficient of Na$^+$ during discharge via GITT curves. **f**, Nyquist plots of A-MoO$_x$ and C-MoO$_x$ in Na$^+$ solution. **g**, Arrhenius plots of ln($R_{ct}^{-1}$) versus 1000/T. **h**, The 3D Bode plot of real area-normalized capacitance ($C_0$) vs. frequency vs. potential. **i**, In-situ Raman shift of A-MoO$_x$ during cycling.
Figure 4

Theoretical calculation of A-MoO$_x$ in intercalation process. a, Structural models for the A-MoO$_x$. b, Na$^+$ migration pathways and corresponding energy barriers in material bulk. c, Charge density difference of A-MoO$_x$ after cation intercalation. d, Adsorption energies of cations over A-MoO$_x$. 
Figure 5

**Electrochemical performance of A-MoO$_x$ based aqueous batteries.** a, Intercalation process schematic diagram during charging/discharging process. b, CV curves of aqueous batteries in various electrolyte. c, GCD plots of Na$^+$ aqueous batteries. d, Cycling performance of aqueous batteries in Na$^+$ solution. e, The relationship between capacitance verses charging rate. f, Ragone plots of the A-MoO$_x$ based aqueous batteries. g, Optical image of LED array powered by two series battery. plots of Na$^+$ aqueous batteries.

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