



Li-ion storage in orthorhombic hydrated sodium molybdate with oxygen-vacancy defects

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ABSTRACT

Two orthorhombic salts (OHMs) of $\text{Na}_2\text{MoO}_4 \cdot (\text{H}_2\text{O})_2$ were prepared at 130 °C (OHMs₁₃₀) and 170 °C (OHMs₁₇₀) via a hydrothermal process, followed by heat treatment. Advanced analyses proved the formation mechanism of the layered structures of unique OHMs. All OHMs possessed layered structures with many empty channels and numerous oxygen vacancies (V_O). V_O were formed due to the absence of O atoms in tetrahedra MoO_4 ($\text{V}_{\text{sh-O}}$) and the loss of H_2O molecules ($\text{V}_{\text{water-O}}$) in the OHMs structure. Despite the micro-sizes of OHMs crystals, the OHMs-based anodes in Li-ion batteries exhibited superior cyclic and rate performance. OHMs₁₇₀ electrode exhibited higher capacity retention (91.6% after 200 cycles) and rate capability (80% at 3 A g^{-1}) than OHMs₁₃₀. It is attributed to the advantageous formation of a higher amount of $\text{V}_{\text{water-O}}$ and a low amount of $\text{V}_{\text{sh-O}}$ in the OHMs₁₇₀ leading to the stable structure of the electrodes and fast Li^+ ion movements during charge/discharge processes. In addition, the electrochemical impedance spectroscopy, Randles-Sevcik equation, and kinetic study results suggested that the exceptional performance of the OHMs₁₇₀ electrode came from low resistance, pseudo behavior, and fast Li^+ mobility inside the OHMs structure.

1. Introduction

The rapid growth of the use of renewable energy and electric vehicles has increased the demand for secondary batteries, especially lithium-ion batteries (LIBs). Therefore, finding abundant and inexpensive anode materials for the mass production of LIBs has become an acute concern. Many types of anode materials have been studied and published in recent years, such as Nb-based materials [1–3], V-based materials [4,5], Sn-based materials [6,7], S-based materials [8–10], and hybrid materials [11,12]. Among LIB anode candidates, molybdate-based materials have gained attention for two reasons: (i) Mo is an industrially abundant element, and (ii) the multivalent states of Mo (up to + 6) promise a high capacity. From 2017 to 2019, the world annually produced ~ 300,000 tons of Mo with a low price of 18–26 USD kg^{-1} , as the main source of Mo was a byproduct of copper production [13]. Transitional metal

molybdates such as FeMoO_4 have the ability to deliver a reversible capacity of 1265 mAh g^{-1} ; however, they often require a lengthy activation time of up to 200 cycles [14,15]. Despite the advantageous short activation time, the reported alkaline/alkaline earth metal molybdates have received little interest because of their low capacities and poor rate performance [16–20]. For example, carbon-coated $\alpha\text{-Na}_2\text{MoO}_4$ nanoplates had a specific capacity of only ~ 380 mAh g^{-1} at 0.03 A g^{-1} and lost ~ 90% of its capacity when the current density increased to 0.5 A g^{-1} . Considering that the performance of an anode material strongly depends on its structure, the following material design strategies have been proposed to improve performance: (i) creating open structures to facilitate the movement of Li^+ ions and (ii) introducing oxygen vacancy defects (V_O) to supply more active sites and improve the intrinsic conductivity and alleviate the volume expansion [21–26]. The appropriate amount of V_O may act as an electronic charge carrier to significantly

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improve the electrical conductivity, lead to promote the ion/electronic transport, and increase Li^+ ion diffusion coefficients [27,28]. In addition, it is believed that V_O serve as the active sites for redox reactions, and the proper concentration of V_O could also increase the capacitance and decrease the generation of insulated Li_2O [22,25,29]. Furthermore, it is considered that V_O induce the formation of the built-in electric field at the atomic level, resulting in significantly enhanced electrochemical performance [30]. Therefore, it was hypothesized that introducing V_O as an anode material for LIBs could be extremely crucial for achieving excellent electrochemical performance. Microcrystals are more readily processable than nanocrystals; however, only a few microcrystals have been demonstrated to be suitable as anodes in LIBs [31–33]. Exceptionally, the defected MnCO_3 microcrystals, which had sizes of 3–4 μm , showed good cyclability and rate performance [34].

In this study, we report the superior lithium storage performance of alkaline metal molybdates by exploiting the open structure of an orthorhombic hydrated molybdate salt (OHM), $\text{Na}_2\text{MoO}_4 \cdot (\text{H}_2\text{O})_2$. Furthermore, we suggest that OHM microcrystals with oxygen vacancies could be promising candidates for fast-charging LIBs.

2. Experimental section

2.1. Material synthesis

After mixing 30 ml of 2.7 wt% Na_2MoO_4 with 10 ml of 7.4 wt% NaOH, the obtained mixture was poured into a dispersion stabilizer prepared by dissolving 0.15 g of poly-(2-ethyl-2-oxazoline) (PEtOx, $M_w = 50\,000$ Da) in 30 ml of 2 wt% polyvinylpyrrolidone (PVP, $M_w = 360\,000$ Da) at different temperatures (130 °C and 170 °C). Subsequently, 40 ml of 4.3 wt% NaBH_4 was slowly added to the aforementioned blended system. After 2 h of reaction, the precipitate was collected via centrifugation and washed with ethanol. The precipitate was annealed at 200 °C for 6 h at ambient pressure after being dried at 70 °C for 4 h in a vacuum oven to remove volatile impurities. Triethylene glycol (TEG) was used as the solvent for the reaction, except for the aqueous NaOH solution. All the reaction and annealing steps used Ar gas to maintain an inert atmosphere.

2.2. Materials characterization

The crystal structure, chemical function, and morphology of the prepared materials were investigated via X-ray diffraction (XRD, Bruker-AXS-D8, Cu K α), Fourier-transform infrared resonance (FTIR) spectroscopy (Bruker Vertex 70, Germany), scanning electron microscope (SEM, JSM-6700F), and transmission electron microscope (TEM, Talos-F200X). X-ray photoelectron spectroscopy (XPS, Kratos AXIS Nova) and inductively coupled plasma mass spectrometry (ICP-MS, NexION®2000) were conducted to determine the elemental composition and chemical state. To perform the structural defect investigation of the prepared materials, nuclear analytical spectroscopy based on the positron–electron pair annihilation was used. The samples were prepared in a sandwich geometry, in which a positron source (^{22}Na , 20 μCi) was placed between two similar sample pellets. For positron annihilation lifetime (PAL) measurements, a fast–fast coincidence spectroscopy (with a time resolution of 220 ps) using two plastic scintillation detectors (Ortec) was used [35]. For Doppler broadening (DB) experiments, an HPGe detector (Ortec) with an energy resolution of 1.5 keV at the 570 keV peak of a ^{207}Bi radioactive source was set up in a low background-lead box to reduce the contribution of background radiation during the experimental process [36]. All PAL and DB spectra were measured under vacuum conditions with a total count of 3×10^6 events. The electron momentum distribution (EMD) curves were converted from the measured DB spectra using the energy conservation rule and they were normalized to the EMD curve of one single-crystal Si [37]. The observed positron lifetime spectra were analyzed into single lifetime components by using LT program [38], while two characteristic S and W parameters

of the DB spectra were detected by using SP program [37].

2.3. Electrochemical characterization

The active materials were mixed with carbon black (Super P) and poly(acrylic acid) (ratio of 70:15:15 wt/wt) in ethanol to form a slurry cast on a Cu foil. The electrodes were dried overnight in a vacuum oven after 3 h pre-drying at ambient pressure at a drying temperature of 70 °C. The mass load of the active material was $\sim 1\text{ mg cm}^{-2}$. The cells were assembled in a glovebox with CR2032-type coin cells, a Celgard 2400 separator, and reference electrodes (Li metal). The electrolyte was 1 M LiPF_6 in ethylene carbonate and diethylene carbonate (1:1 v/v). A battery cycler system (Arbin Instrument, BT2143) was used to perform cyclic voltammetry (CV) and galvanostatic cycling tests in the potential range of 0.01–3 V. The rest time before the galvanostatic cycling was 10 h. Electrochemical impedance spectroscopy (EIS) was conducted on a VSP multichannel potentiostat/galvanostat (Biologic) from 100 kHz to 100 mHz. CV tests were conducted after five cycles at various scanning rates from 0.3 to 1.2 mV s^{-1} in the potential range of 0.01–3.00 V on an Arbin Instruments BT2143 to calculate the Li^+ diffusion coefficients and to perform the kinetics study of the electrodes. All capacity calculations in this study were based on active materials.

3. Results and discussion

Fig. 1 presented a schematic of the formation of OHMs via a hydrothermal process and the unique open structures formed by introducing V_O defects. NaO_6 octahedra were formed in TEG medium with the assistance of PVP, PEtOx, and NaOH. Conventionally, MoO_4 tetrahedra can attract NaO_6 octahedra to form Na_2MoO_4 as an intermediate product. In addition, MoO_4 tetrahedra might also react with NaBH_4 , as Tsang and Manthiram reported in 1997 [39]. They reported that MoO_4 tetrahedra were reduced by NaBH_4 to form as-generated H_2 and components consisting of Mo with a low oxidation state (MoO_{4-x}). A strong alkaline environment is indispensable in preventing the rapid loss of H_2 and the gradual condensation of MoO_4 tetrahedra during the reaction [39]. Therefore, a high concentration of NaOH was used in this study.

Accordingly, in the process (Fig. 1a), if H_2 was introduced via NaBH_4 hydrolysis, the as-generated H_2 could compete for binding to NaO_6 octahedra at O positions to form Na_2O_9 polyhedra consisting of NaO_6 hexahedra linked with NaO_6 octahedra and H_2O (Fig. 1(a,b)). Ultimately, the as-generated H_2O and oxygen in the MoO_4 tetrahedra could be removed at high temperatures, resulting in the formation of V_O (including both $\text{V}_{\text{water-O}}$ and $\text{V}_{\text{sh-O}}$) while the crystal continued to grow (Fig. 1c). Nevertheless, because NaBH_4 hydrolysis strongly relied on temperature, it was essential to determine the appropriate reaction conditions. In this study, the samples were prepared at specific temperatures, 130 °C and 170 °C (i.e., OHMs₁₃₀ and OHMs₁₇₀, respectively) for three reasons: Firstly, OHM's synthesis at above 170 °C can be dangerous due to H_2 gas generation during the reaction. Secondly, undesired byproducts and transfer phases could be formed at higher temperatures. Thirdly, many studies have suggested that vacancies become unstable at elevated temperatures while they are almost stable at low temperatures [35,40,41]. In addition, a sample was prepared at 90 °C (marked as CM₉₀) as a comparison sample. As the crystal structures of materials are frequently responsible for the mobility of Li^+ ions, the deliberation of the OHM structure may forecast the electrochemical performances of the prepared OHMs. In Fig. S1, the cubic structure of Na_2MoO_4 signified the hard movement of Li^+ ions within its structure. In fact, NaO_6 octahedra in $\alpha\text{-Na}_2\text{MoO}_4$ with a cubic structure blocked the 3D channels because the Na species were considerable stationary parts during the Li^+ insertion [18]. The OHMs that had an orthorhombic structure consisted of many empty channels, as shown in Fig. 1b. These empty channels facilitated the movement of Li^+ ions and provided space in which to suppress volume expansion during the charging/discharging processes. Furthermore, the formation of numerous V_O in the OHM

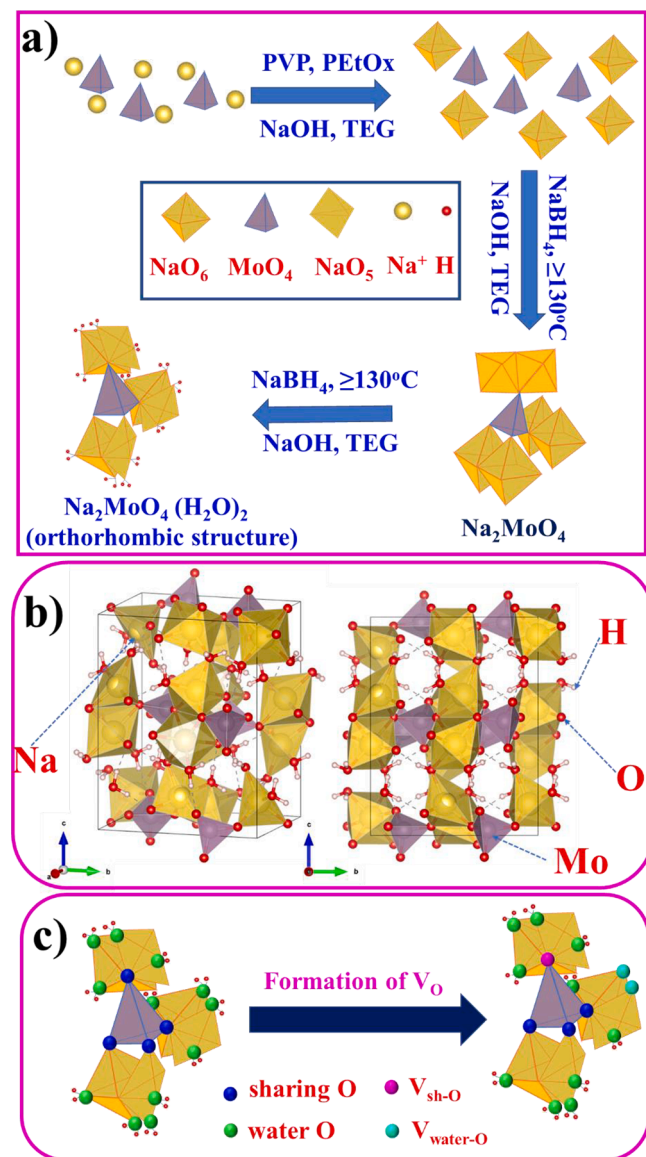


Fig. 1. (a) Scheme for formation of OHMs and (b) crystallographic structure of $\text{Na}_2\text{MoO}_4 \cdot (\text{H}_2\text{O})_2$. (c) Formation of oxygen vacancies in the OHM materials.

materials provided considerable empty spaces that were favorable for the fast movement of Li^+ ions and the alleviation of volume change during cycling (Fig. 2). Especially, these functions present many advantages, such as more spaces for Li^+ ions' absorption and more channels for Li^+ ions transport when the amount of $V_{\text{water-O}}$ is higher than amount of $V_{\text{sh-O}}$ in the OHMs materials as shown in Fig. 2a. Therefore, the Li^+ storage performance of the prepared OHMs with V_O was expected to be superior to that of the reported cubic structure ($\alpha\text{-Na}_2\text{MoO}_4$) owing to their 3D channels and layer structures.

XRD analysis of the OHM powders (Fig. 3(a,b)) verified that the structure of OHMs_130 and OHMs_170 matched well with the reported orthorhombic $\text{Na}_2\text{MoO}_4 \cdot (\text{H}_2\text{O})_2$ phase (PDF#70–1710). In Fig. 3c, FTIR spectra indicated that the OHM samples consisted of distinct functional groups of OHMs. For instance, the broad peaks at $\sim 3310\text{ cm}^{-1}$ and medium peaks at $\sim 1680\text{ cm}^{-1}$ represented the symmetric stretching and bending modes of H_2O vibrations [42]. Meanwhile, the sharp peaks at $830\text{--}900\text{ cm}^{-1}$ exhibited the symmetric and asymmetric vibrations of the MoO_4 tetrahedra. SEM images (Fig. 3(d,e)) indicated that both OHMs_130 and OHMs_170 contained octahedral microcrystals with edge lengths of $1.2\text{--}2.6\text{ }\mu\text{m}$.

However, both OHMs_130 and OHMs_170 samples were damaged by the high-energy electron beam used in TEM, as shown in Fig. 3(f,g) and Fig. S2. The OHMs sample was a hydrated salt, and the electron beam accelerated its dehydration. Considering that in-depth characterization of $V_{\text{sh-O}}$ and $V_{\text{water-O}}$ in OHMs was challenging using conventional methods such as XRD, SEM, and TEM, we conducted positron annihilation spectroscopy (PAS), including PAL, DB, and EMD measurements. Fig. 3h and Fig. S3a depicted the PAL and DB spectra, respectively, while Fig. 3i showed the EMD curves. The analyzed PAL data were listed in Table S1, whereas the values for the two characteristic S and W parameters of the DB measurement were presented in Table S2. The correlated plot of the S and W parameters was shown in Fig. S3b. Our analysis of the positron annihilation experiments provided in Supplementary Information (SI) indicated the following results. First, OHMs_130 and OHMs_170 contained not only monovacancies and vacancy clusters but also some nanopores with an average size of approximately 0.6 nm (approximately twice the size of a H_2O molecule), in agreement with the dehydration under the electron beam seen using TEM and the observations in Fig. 3(f,g). The number of nanopores in OHMs_170 was found to be higher than that in OHMs_130. This finding was confirmed by the PAL analysis. Second, DB analysis suggested that OHMs_130 and OHMs_170 had the same defect type and MoO_3 had a different type of defect and that the concentration of defects in OHMs_170 was higher than that in OHMs_130. Third, EMD analysis confirmed that oxygen vacancies (V_O) in OHMs_130 and OHMs_170

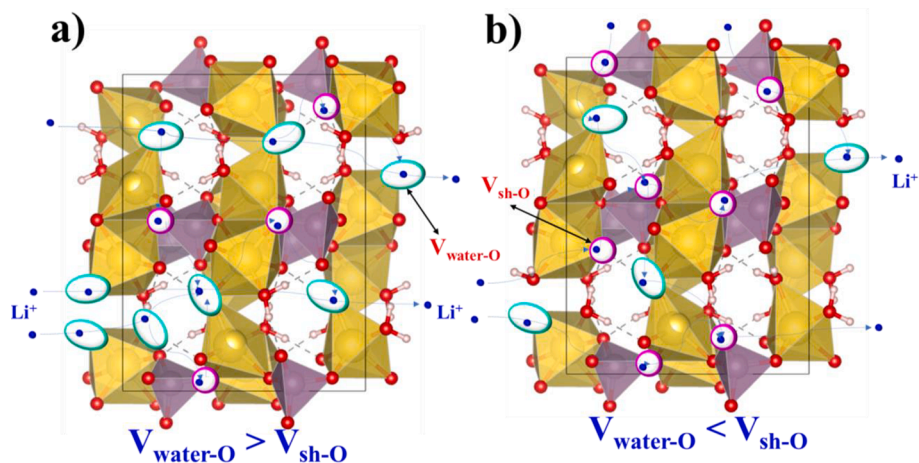


Fig. 2. Scheme for the different functions of oxygen-vacancy defect-types in the OHMs materials as anodes for LIBs in the case (a) $V_{\text{water-O}} > V_{\text{sh-O}}$ and (b) $V_{\text{water-O}} < V_{\text{sh-O}}$.

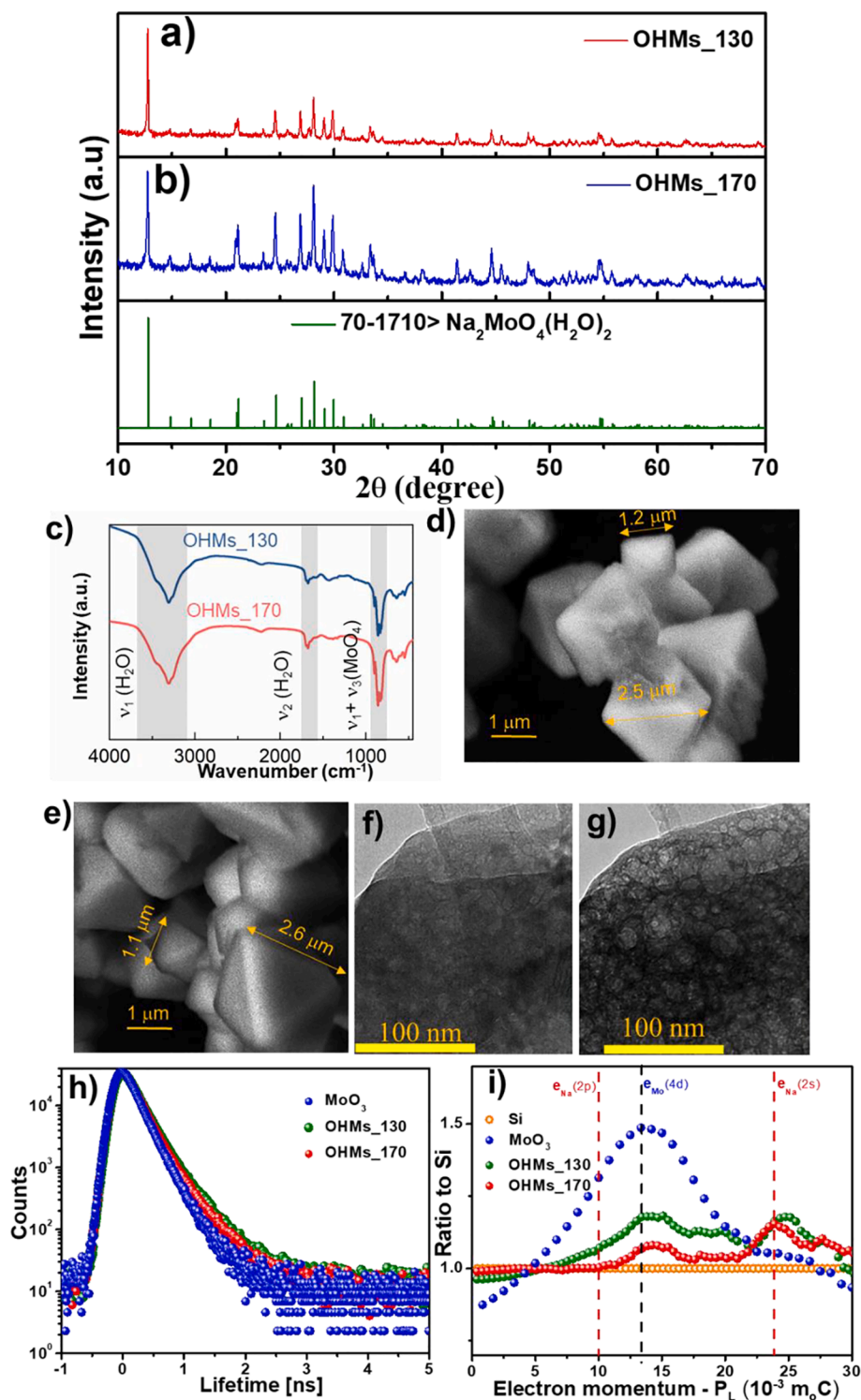


Fig. 3. XRD patterns of (a) OHMs_130 and (b) OHMs_170. (c) FTIR of OHMs samples. SEM images of (d) OHMs_130 and (e) OHMs_170. TEM images of OHMs_170 at (f) 10 s and (g) 20 s after reaching specific resolution. (h) Positron lifetime spectra, and (i) EMD curves of OHMs samples. Note that EMD curves were normalized using one single-crystal Si.

were caused by the loss of O sharing ($V_{\text{sh-O}}$) and O in water ($V_{\text{water-O}}$), as well as that the number of $V_{\text{sh-O}}$ in OHMs_170 was smaller than that in OHMs_130. The above-mentioned properties of OHMs_170, in particular, the small number of $V_{\text{sh-O}}$ and high number of $V_{\text{water-O}}$ in OHMs_170, as shown in Fig. 2a, led to a significant improvement in the ion-exchange properties of this material. It was attributed that those vacancies could provide more empty spaces for the absorption of Li^+ ions and strongly promoted the reactions of Li^+ ions with MoO_4

tetrahedra and Na_2O_9 polyhedra as shown in Fig. 2.

XPS analysis was conducted to confirm the existence of V_{O} and determine the oxidation state of the elements in the OHMs samples. The associated results were presented in Fig. 4 and Fig. S4, which clearly showed that the survey spectra of the OHM samples were similar to each other and revealed the existence of Mo, Na, and O (Fig. 4a and 4e). The fitting curves of $\text{O } 1s$ (Fig. 4b and 4f) were presented in the form of three distinct peaks at 530.1 eV, 531.3 eV, and 532.6 eV. The peak at 530.1 eV

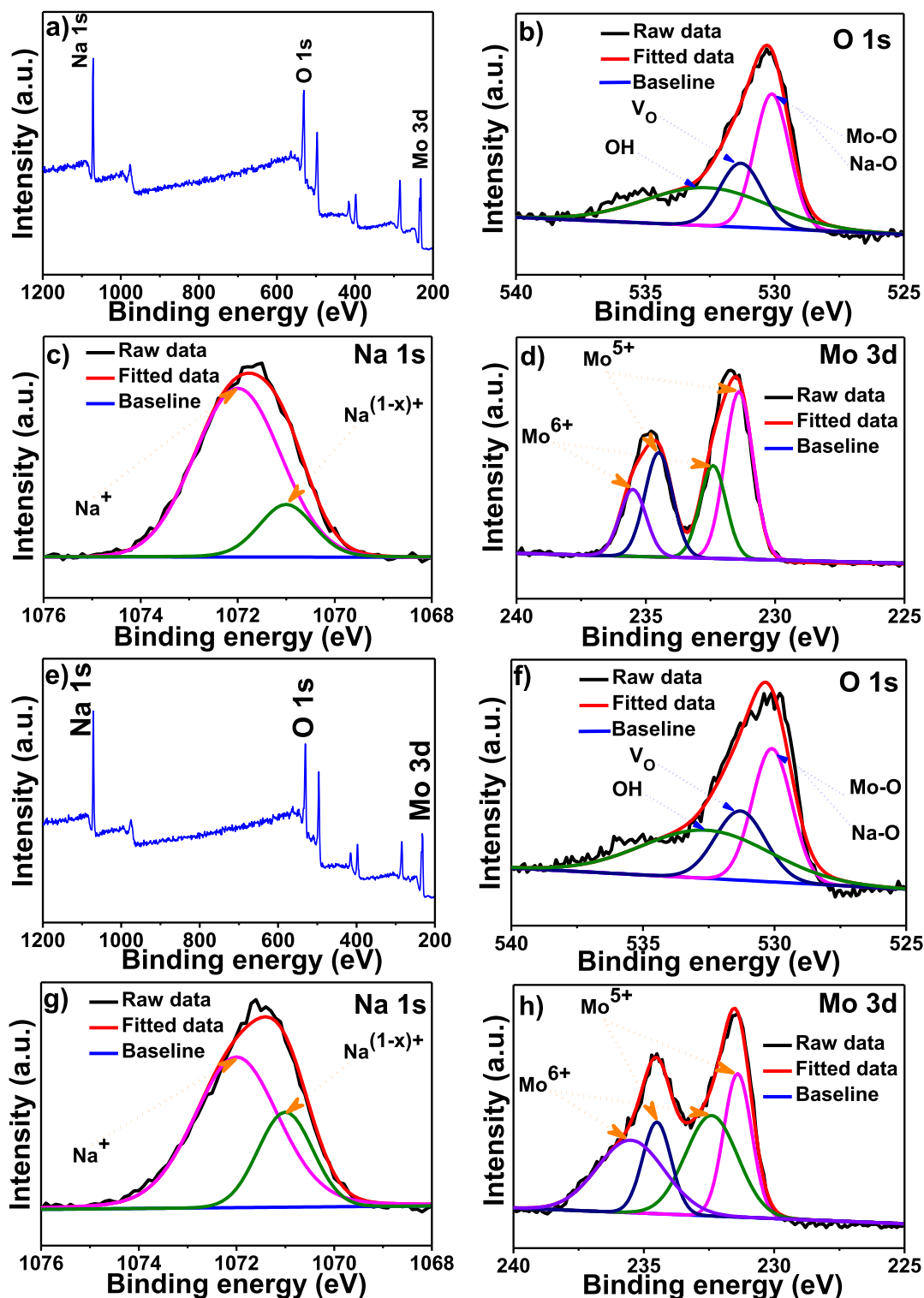


Fig. 4. XPS profiles of (a–d) OHMs_130 and (e–h) OHMs_170 samples.

could be ascribed to $(\text{MoO}_4)^{2-}$ in M–O (Mo–O and Na–O) bonds [43–45]. The peak located at 531.3 eV could be assigned to the presence of V_O inside the OHMs samples [35,46–48]. Finally, the peak at 532.6 eV could be attributed to the existence of OH groups [48,49] from H_2O in the OHMs samples. There were numerous V_O and H_2O molecules in all samples, which was in agreement with the XRD, FTIR, and EMD analyses. The area ratio between V_O and M–O in the XPS spectra of O 1s was calculated to be 0.58 and 0.66 for OHMs_130 and OHMs_170, respectively. This implied that the amount of V_O in OHMs_170 was higher than

that in OHMs_130. This result was consistent with the DB results (Fig. S3a). The high resolution of the Na 1s spectra (Fig. 4c and 4g) showed a large peak at 1072 eV and a small peak at 1071 eV, indicating the existence of both Na^+ and $\text{Na}^{(1-x)+}$ in the OHMs samples, respectively [50]. As shown in the spectral analysis of Mo 3d (Fig. 4d and 4h), the peaks at 232.4 eV and 235.5 eV were assigned to $\text{Mo}^{6+} 3d_{5/2}$ and $3d_{3/2}$, respectively [43,51], while two peaks at 231.4 eV and 234.5 eV corresponded to $\text{Mo}^{5+} 3d_{5/2}$ and $3d_{3/2}$ in $(\text{MoO}_4)^{2-}$, respectively [52,53]. The Mo^{5+} and $\text{Na}^{(1-x)+}$ in the OHM materials were formed through the

partial reduction of Mo and Na atoms by electrons trapped around V_O [54–56]. It was interesting that the area ratio between the $Na^{(1-x)+}$ and Na^+ peaks in the XPS profile of OHMs_170 was two orders of magnitude larger than that of the OHMs_130, while the area ratio between the Mo^{5+} and Mo^{6+} peaks of OHMs_170 was approximately 4.6 orders of magnitude lower than that of OHMs_130, as shown in Table S4. These results indicated three facts: (i) the V_O in OHMs samples included both V_{sh-O} and $V_{water-O}$, (ii) the amount of V_{sh-O} in OHMs_170 was lower than that in OHMs_130, and (iii) the amount of $V_{water-O}$ in OHMs_170 was higher than that in OHMs_130, which was verified using EMD analysis. Furthermore, the composition of the elements in the OHM materials determined by XPS analysis (Table S5) showed that the amount of O in OHMs_170 was lower than that in OHMs_130, whereas both the amount of Na and Mo in OHMs_170 was higher than that in OHMs_130. These results support the different formation mechanisms of $V_{water-O}$ and V_{sh-O} in the two OHMs. The existence of considerable V_{sh-O} and empty spaces in the OHM structure promotes the absorption of Li^+ ions around the MoO_4 tetrahedra, and, consequently, the fast reactions of Li^+ ions with MoO_4 tetrahedra. The formation of V_{sh-O} led to a decrease in the oxidation state of Mo^{6+} in MoO_4 tetrahedra to become Mo^{5+} , resulting in a decreased capacity. The presence of many $V_{water-O}$ created a large number of nanopores on the surface of the OHM materials, increasing the absorption of Li^+ ions around the Na_2O_9 polyhedra. The generation of $V_{water-O}$ also led to a decrease in the state of Na^+ in the Na_2O_9 polyhedra. This decrease could improve the capacity for the following reasons: (i) Na^+ ions did not react with Li^+ ions; therefore, it did not affect the capacity significantly; (ii) the removal of H_2O molecules formed nanopores, which could absorb many Li^+ ions, leading to an increased contribution ratio for the pseudo-process; (iii) the loss of H_2O in the structure of OHM materials led to a decrease in the weight of OHMs materials, resulting in a capacity increase. Moreover, there were lopsided charge distributions with V_O leading to a local electric field in the OHMs because the center zone of V_O possessed a positive charge, while a negatively charged zone was around V_O [30]. During the discharge process, the electric field formed between the defect-free zone and the negatively charged zone could increase the migration of Li^+ ions to the V_O zone due to Coulombic forces. The negatively charged zone became electrically neutral after the completion of lithiation. In contrast, during the charging process, the second electric field formed from the center zone of V_O to the electroneutral lithiation layer, which was distributed around V_O , could promote the extraction of Li^+ ions, resulting in a fast-charging process for the OHM electrodes [25,30,57]. The different amounts of V_{sh-O} and $V_{water-O}$ in the OHM materials were a significant factor for the excellent electrochemical performance of the OHM electrodes as shown in Fig. 2.

To further understand the properties of the OHMs materials and provide strong evidence for the existence of V_O in the OHMs materials, Raman analysis and Rietveld refinement on the XRD patterns of the prepared samples were performed. The results were presented (Fig. S5 and Fig. S6) and discussed in more detail in SI. Moreover, the effect of reaction temperatures and oxygen-vacancy defect-types on the specific surface area and pore-size distributions of the OHMs materials were determined by Brunauer-Emmett-Teller (BET) tests as shown in Fig. S7. The OHMs_170 material presents a specific surface area of $38.7 \text{ m}^2 \text{ g}^{-1}$ with a dominant pore size distribution at 39.6 nm (Fig. S7d), whereas the OHMs_130 material only shows a specific surface area of $25.4 \text{ m}^2 \text{ g}^{-1}$ with a pore size distribution almost at 18.9 nm (Fig. S7c). It is clear that the OHMs_170 material possesses a higher surface area (1.5 times) and larger pore size (2.1 times) than the OHMs_130 material, which could be due to the existence of a larger amount of $V_{water-O}$ in the OHMs_170 structure than the OHMs_130 material. These results are consistent with PAS and XPS results as well as the scheme shown in Fig. 2. Because of the greater loss of H_2O molecules during the synthesis, the OHMs_170 possesses a high surface area and large pore size. These characteristics provide a larger number of channels for fast Li-ion transports, a decrease in the volume expansion, and an increase in the contact areas between

the active materials and the electrolytes.

CV results showed that OHMs_130 had the typical redox peaks of an alkaline metal molybdate (0.01–3 V) (Fig. 5a). For instance, during the first discharge, the cathodic peak at 1.06 V presented the first lithiation, accompanied by the partial reduction of the Mo species from the highest oxidation states (+6 and +5) to intermediate ones such as +5 and +4 [16]. The cathodic peak at 0.54 V could be related to the solid-electrolyte-interface (SEI) formation, which disappeared later. Further lithiation occurred with the complete reduction of the Mo species to their lowest oxidation state (Mo^0) below 0.5 V, which frequently resulted in unclear peaks [18]. The anodic peaks at 0.58 V, 0.94 V, 1.17 V, and 1.50 V corresponded to multistage reactions, including phase transformation and the oxidation of Mo^0 to Mo^{+4} and Mo^{+5} [17]. According to the XPS evidence provided by X. Liu et al., the complete delithiation of lithiated molybdate was barely reached via charging owing to the inability to restore Mo^{+6} at the fully charged state of the electrode [17]. Because of the depletion of Mo^{+6} after the first cycle, the cathodic peak shifted from 1.06 V to 0.90 V from the second cycle. Fig. 5b revealed that OHMs_170 also exhibited similar redox reactions to OHMs_130 during lithiation/delithiation. However, a new cathodic peak existed at 1.40 V in the first cycle and shifted to 1.20 V starting in the second cycle. The high amount of $V_{water-O}$ in OHMs_170 might force the first lithiation to occur earlier at a higher potential than in OHMs_130. It was interesting that the reversible capacities of both the OHMs_130 and OHMs_170 electrodes (Fig. 5c and Fig. S8) were higher than the theoretical capacity of $Na_2MoO_4 \cdot (H_2O)_2$ (665 mAh g^{-1}), which could be due to the loss of both H_2O and O to form V_O in the OHMs structures, leading to a decrease in the molecular weight of the OHMs materials and contributing to an increase in the capacity. Moreover, the initial Coulombic efficiency (ICE) of the OHMs_170 electrode (87.4%) was much higher than that of the OHMs_130 electrode (63.9%) and other molybdate-based systems (Fig. 5c and Fig. 5d), indicating the positive effect of V_O in the OHM materials. For instance, the ICE of electrodes prepared from $CaMoO_4$, Li_2MoO_4 , and $\alpha\text{-Na}_2MoO_4$ seldom exceeded 70% regardless of morphology and the conductive coating layers (Fig. 5d) [16–20]. The high ICE of OHMs are most likely attributed to the existences of V_O based on the following reasons: (i) the existences of V_O led to decrease the conversion reactions (not reversible perfectly) between metal oxides and Li^+ ions; (ii) V_O could provide more empty spaces for Li^+ ions' absorption (high reversible capacity) and strongly promote Li^+ ions' reactions with MoO_4 tetrahedra and Na_2O_9 polyhedra (i.e., greater contribution of the pseudo-process). Therefore, V_O not only decreased the conversion reactions but also increased the contribution of the pseudo-process, leading to an improvement of both ICE and Coulombic efficiency during cycling.

Fig. 6a demonstrated that the OHMs_170 electrode possessed better long-term cyclability than the OHMs_130 electrode. After 200 cycles, the capacity of the OHMs_170 was 710 mAh g^{-1} , corresponding to a capacity retention of 91.6%. Likewise, the OHMs_130 electrode reached a specific capacity of 485 mAh g^{-1} , or a capacity retention of 70.3%. Clearly, the OHMs-based electrodes in this work exhibited a better cyclability than the reported $\alpha\text{-Na}_2MoO_4$ electrode, which delivered a capacity of 200 mAh g^{-1} , or a capacity retention of 66.7%, at 0.03 A g^{-1} after 29 cycles [18]. In addition, because OHMs_170 was more adaptable to volume change than OHMs_130 due to the large size of $V_{water-O}$ (Fig. 2), the longevity of the OHMs_170 electrode exceeded that of the OHMs_130 electrode. We compared the electrochemical properties of OHMs_170 electrode in this work with the recent studies on Mo-based anodes in Table S7, which exhibits the superior performance of OHMs_170. In addition, the changes in the morphology of the OHM electrodes after 200th cycles were investigated by *ex situ* SEM and presented in Fig. S9 with the detailed discussion. Fig. 6b revealed the dependence of reversible capacities of OHMs-based electrodes on the withdrawn/applied current density. Noticeably, the OHMs_130 electrode lost 30.4% of its specific capacity (from 690 mAh g^{-1} to 480 mAh g^{-1}) when the current density increased from 0.1 A g^{-1} to 3 A g^{-1} . At the

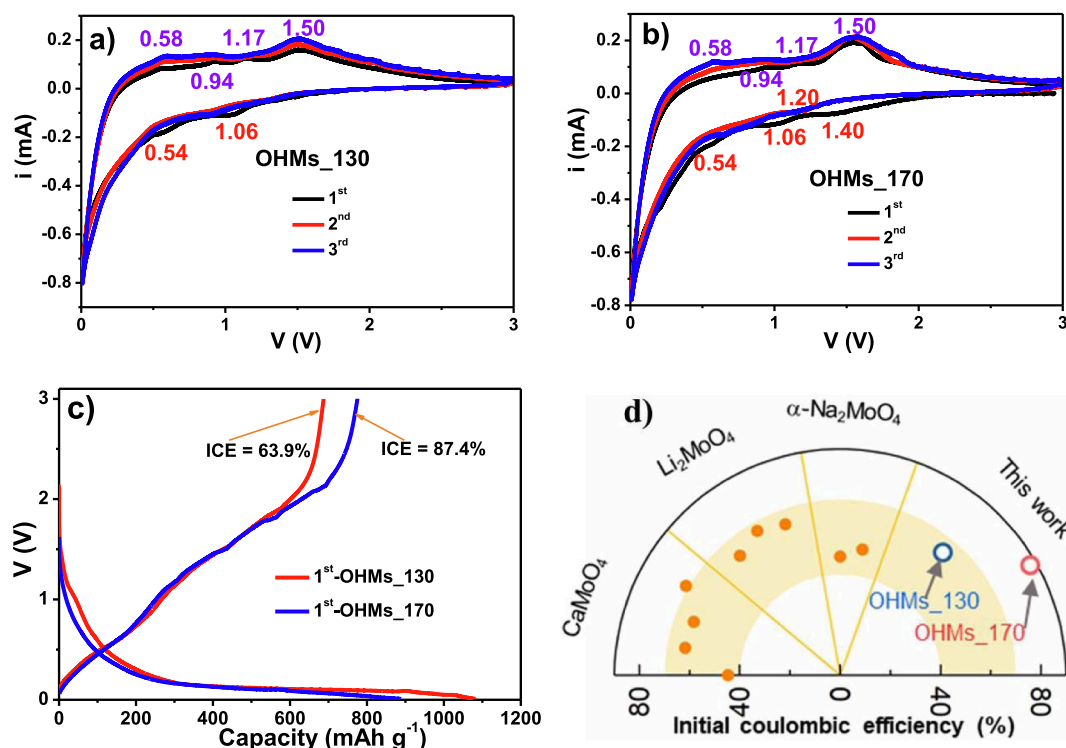


Fig. 5. CV of electrodes prepared from (a) OHMs_130 and (b) OHMs_170; (c) voltage profiles of OHMs electrodes in the first cycle; (d) comparison of initial coulombic efficiency of electrodes prepared from various alkaline/alkaline earth molybdates.

same time, the capacity loss of the OHMs_170 electrode was only 20.9% (from 790 mAh g^{-1} at 0.1 A g^{-1} to 625 mAh g^{-1} at 3 A g^{-1}). Interestingly, OHMs-based electrodes reached a better rate cyclability than that of other reported molybdate-based electrodes despite the micro size of the as-prepared OHMs (Fig. 6c). Even with the support of the carbon coating layers, the specific capacities of conventional molybdate-based electrodes at 3 A g^{-1} barely sustain 30% of their capacities at 0.1 A g^{-1} [16,18,58]. Despite the similar chemical formulae of the molybdate salts, the tremendous difference in rate cyclability undoubtedly came from the structural distinction and the presence of V_O . Additionally, the comparison sample synthesized at 90°C (CM_90) was investigated and its morphology, crystal structure, and electrochemical performances were presented and discussed in SI (Fig. S10, Fig. S11).

Owing to the exceptional performance of OHMs electrodes, it was essential to ascertain its electrical resistances and the Li^+ mobility via an EIS test. The semicircles of OHMs_170 electrode were markedly smaller than those of OHMs_130 electrode, as shown in Fig. S12a, whereas the slope of an inclined line at a low frequency region in the OHMs_170 electrode was higher than that of OHMs_130 electrode, indicating that Li^+ ions move faster in the OHMs_170 electrode. The equivalent circuit for the Nyquist plots of the OHMs electrodes was a modified Randles circuit containing series resistance (R_s), SEI resistance (R_{SEI}), charge-transfer resistance (R_{CT}), capacitance (C) and Warburg elements (W), as shown in Fig. S12b. The real part of the total impedance (Z') is a function of the angle frequency (ω) as shown in Eq. S1. It was interesting that the relationship between Z' and $\omega^{-1/2}$ in the low frequency zone was linear, where the slope assigned to Warburg coefficient (σ) and the intercept corresponded to the total resistance ($R_s + R_{\text{SEI}} + R_{\text{CT}}$), which could be determined easily as shown in Fig. 6d. The σ value of the OHMs_130 electrode was 1.16 times of magnitude larger than that of the OHMs_170 electrode. When using Eq. S2 to estimate the diffusion coefficient (D) of the Li^+ ion in the OHMs electrodes, the D value for the OHMs_170 electrode was 1.35 times of magnitude higher than that of OHMs_130 electrode. The faster movement of Li^+ ions in the OHMs_170 electrode led to excellent rate capability and superior electrochemical

performance. The fitting of the Nyquist plots following the model in Fig. S12b and the resistance of the components were presented in Fig. 6e and Table S8, respectively. It was clear that all resistance values for the OHMs_130 electrode, such as R_s , R_{SEI} and R_{CT} , were larger than those of the OHMs_170 electrode, and the differences in the resistances between the experimental and fitting values were small, indicating the correction of the fitting model (Table S8). The lowest resistance of the OHMs_170 electrode could be attributed to the open structures and the existence of V_O , especially the presence of a large amount of $V_{\text{water-O}}$ in OHMs_170 [27,28]. These structural characteristics helped the SEI layer and structure of the electrodes to be stable during cycling, which was also beneficial for the penetration of the electrolyte [59,60].

For a better understanding of the diffusion phenomena, the diffusive and pseudo curves of the OHM electrodes were determined at every scan rate using Eq. S3 combined with solving matrix S6 in SI. These curves were shown in Fig. S13, Fig. S14 and Fig. 7(a,b). It was interesting that the CV curves at each scan rate were successfully separated into diffusive and pseudo curves by applying the mathematical method used to solve matrix S6. The contribution ratios of the pseudo and diffusive processes were calculated from the areas of these curves at each scan rate in Table S9 using Eq. S7 and Eq. S8, and the results were presented in Fig. 7(c,d). It was interesting that the contribution ratios of the diffusive process in the OHMs_170 electrode were always larger than those of the OHMs_130 electrode at the same scan rate. For example, the pseudo and diffusive contributions at a scan rate of 1.2 mV s^{-1} were 61.5% and 38.5%, respectively, in the OHMs_130 electrode and 53.6% and 46.4%, respectively, in the OHMs_170 electrode. The diffusive process in the OHMs_170 electrode was higher than that of the OHMs_130 electrode, which could be related to the different amounts of $V_{\text{sh-O}}$ and $V_{\text{water-O}}$ between OHMs materials (Fig. 2). The amount of $V_{\text{sh-O}}$ of OHMs_170 was lower than that of OHMs_130; therefore, the lithiation process of the OHMs_170 electrode was not favorable, as in the case of the OHMs_130 electrode, because the diffusion of Li^+ ions into perfect MoO_4 tetrahedra of OHMs_170 experiences considerable resistance and requires much time to react with the MoO_4 tetrahedra. In contrast, OHMs_130

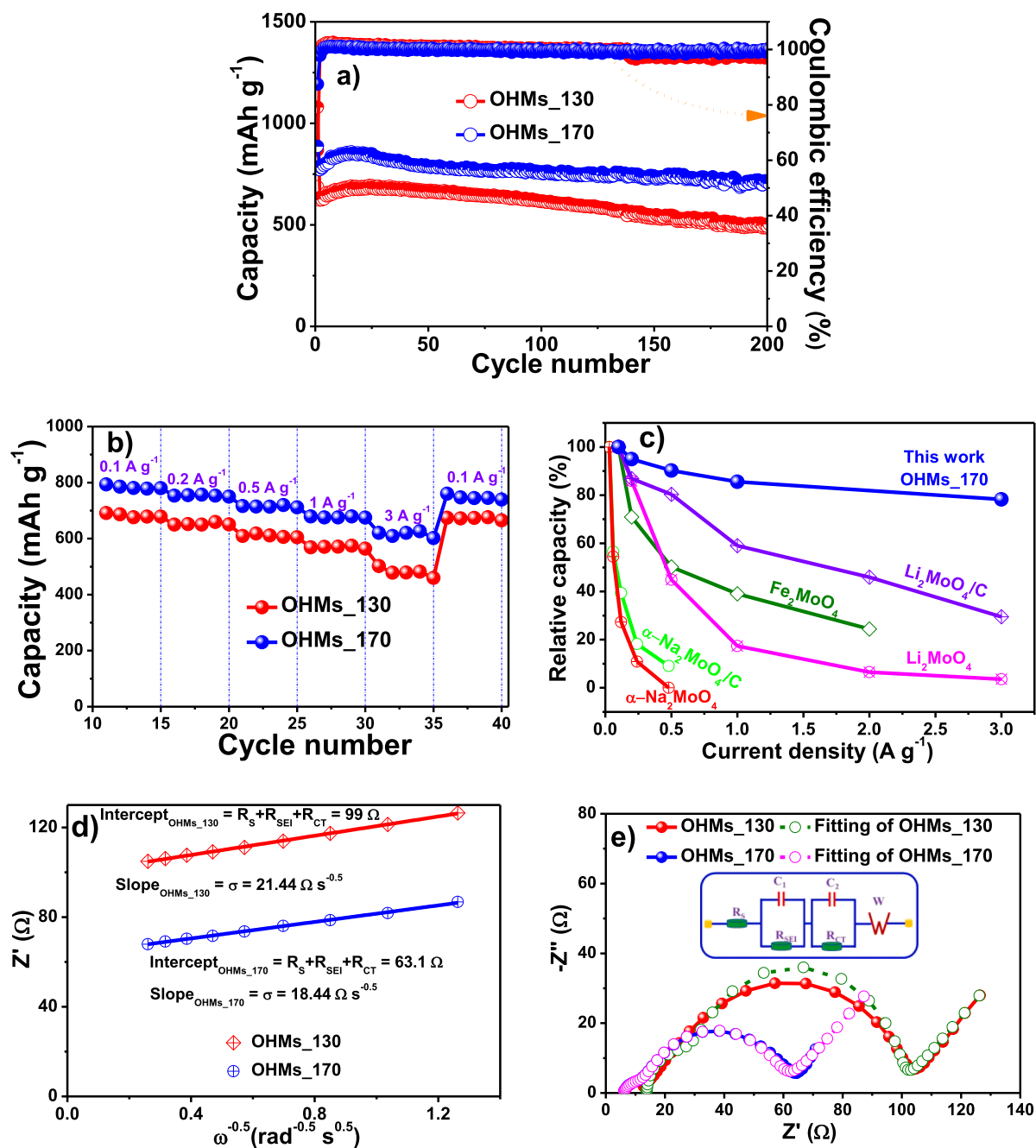


Fig. 6. (a) Long-term cyclability and (b) rate performance of OHMs-based electrodes; (c) comparing rate performance among selected molybdate-based electrodes. (d) Linear relationship of real parts of total impedance vs $\omega^{-1/2}$, and (e) Nyquist plots and fitting of Nyquist plots (inset: the equivalent circuit) for OHMs-based electrodes.

contained a large amount of V_{sh-O} , illustrating that the OHMs₁₃₀ electrode showed a lower capacity than the OHMs₁₇₀ electrode, and the lithiation process occurred quickly. To correctly evaluate the D value for the anodic peaks, the CV curves of the anodic peaks must have been de-polarized by removing the Ohmic resistance (Fig. S15) [61].

The CV curves of the anodic peaks after de-polarization were shown in Fig. 7(e,f). These curves showed that the intensity of the anodic peaks (i_p) at 1.50 V changes as a function of the scan rate (ν). Regarding the Randles-Sevcik equation (Eq. S9), the square root of D was directly proportional to K, which is the slope of the $\nu^{0.5}$ - i_p graph. In Fig. 7g, because the line of the OHMs₁₇₀ electrode ($K_{OHMs_{170}} = 0.03358 \text{ As}^{0.5}\text{V}^{-0.5}$) was steeper than that of the OHMs₁₃₀ electrode line ($K_{OHMs_{130}} = 0.02491 \text{ As}^{0.5}\text{V}^{-0.5}$), the value of D in OHMs₁₇₀ was approximately 1.75 times of magnitude that in OHMs₁₃₀ using Eq. S10

for calculations. This result was also suitable for the calculation of the D value for the OHM electrodes from the EIS study in Fig. 6d and Eq. S2. Therefore, the increase in the diffusivity may have made the OHMs₁₇₀ electrode outperform the OHMs₁₃₀ electrode in the rate test.

It was worth noting that the contribution ratios of the pseudo processes of the OHMs₁₃₀ electrode were always larger than those of the OHMs₁₇₀ electrode, while the D value of the OHMs₁₃₀ electrode was smaller than that of the OHMs₁₇₀ electrode. To determine the exact reason for this, we separated the pseudo and diffusive curves of OHMs electrodes at a scan rate of 1.2 mV s^{-1} into two potential zones; one from 0.01 V to 1.00 V, where the capacity contribution was almost discharge process, and the other from 1.00 V to 3.00 V, where the capacity contribution was dominated by charge process. The contribution ratios of the pseudo and diffusive processes at each potential zone were

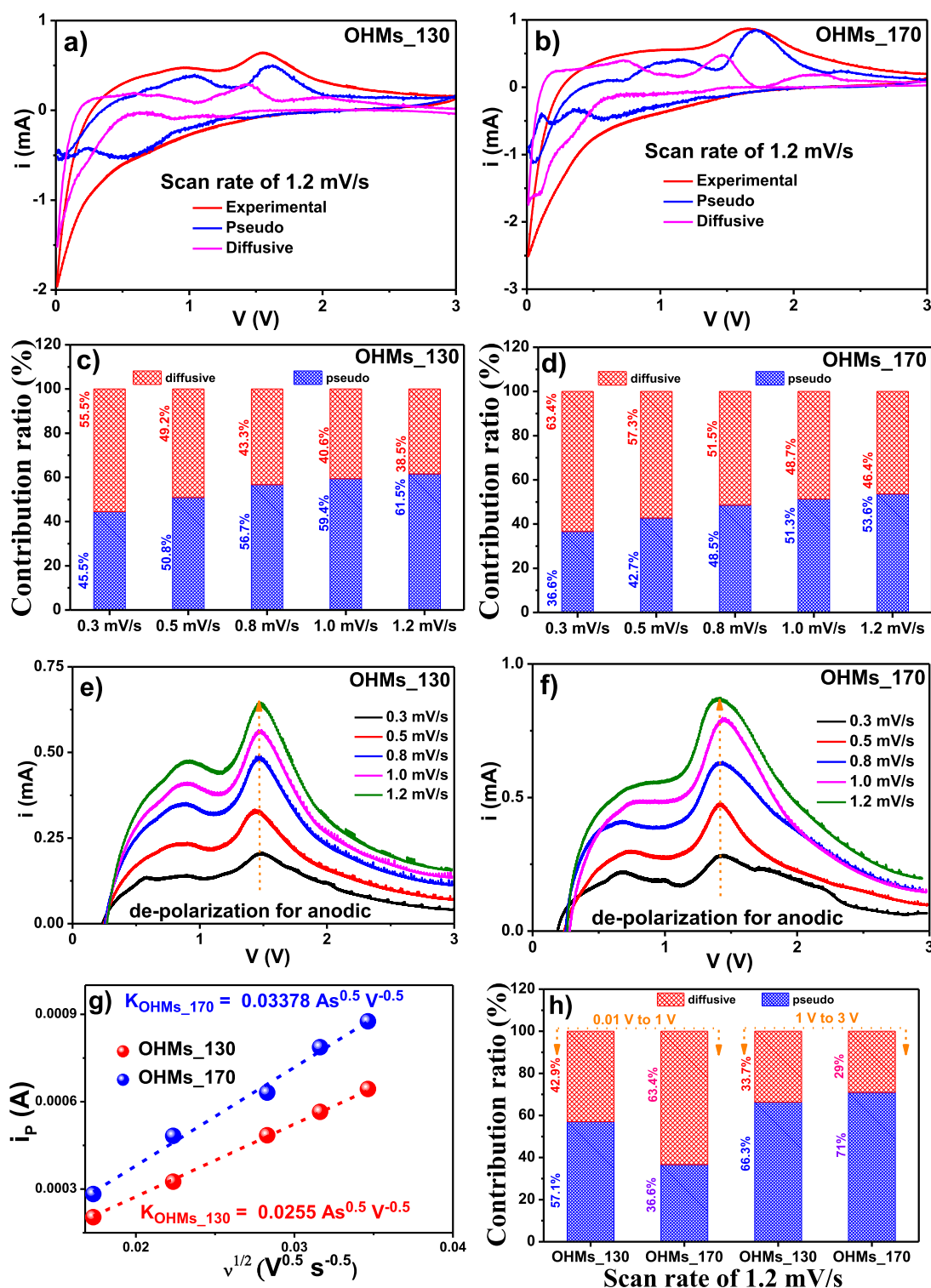


Fig. 7. CV, pseudo, and diffusive curves at scan rate of 1.2 mV/s for (a) OHMs_130 and (b) OHMs_170 electrodes. Diffusive and pseudo contribution at various scanning rates for (c) OHMs_130 and (d) OHMs_170 electrodes. De-polarization CV of anodic peaks for (e) OHMs_130 and (f) OHMs_170 electrodes. (g) Correlation between i_p and $v^{1/2}$. (h) Pseudo and diffusive contribution in the different potential zones at scan rate of 1.2 mV s⁻¹ of OHMs-based electrodes.

calculated and were presented in Fig. 7h. The potential zone from 1.00 V to 3.00 V contained an anodic peak, which was used to compare the D value of the OHMs electrodes (Fig. 7(e,f)). The contribution ratio of the pseudo process for the OHMs_170 electrode was clearly larger than that of the OHMs_130 electrode in this potential zone. This result was suitable for the D values of the OHM electrodes, confirming the faster movement of Li⁺ ions in the OHMs_170 electrode compared to that of

the OHMs_130 electrode during charging. In addition, the different contribution ratios of the pseudo processes between the two potential zones were 9.2% and 34.4% for the OHMs_130 and OHMs_170 electrodes, respectively (Fig. 7h). A large difference in the pseudo process (34.4%) between the two zones occurred in the OHMs_170 electrode. This implied that the diffusive process was dominant in the discharge process, whereas the pseudo process was strongest in the charge process,

illustrating that the contribution ratio of the pseudo process was not high during the charge/discharge process in the OHMs₁₇₀ electrode compared to the OHMs₁₃₀ electrode. The OHMs₁₇₀ material consisted of many perfect MoO₄ tetrahedra; therefore, the reactions between Li⁺ ions and MoO₄ tetrahedra required considerable time for the diffusion of Li⁺ ions into MoO₄ tetrahedra and charge transfer processes, which confirmed that the diffusive process was dominant in the discharge process. However, during the charge process, the movement of Li⁺ ions out of the OHMs₁₇₀ structure was favorable due to the existence of a large amount of V_{water-O}, which fully absorbed many Li⁺ ions during discharge. This was attributed to an important role of the oxygen vacancies in the increasing contribution ratios of the pseudo process [25,29]. The OHMs₁₇₀ structure consisted of more V_{water-O} than the OHMs₁₃₀ structure, and the contribution ratio of the pseudo process for the OHMs₁₇₀ electrode was higher than that of the OHMs₁₃₀ electrode during charging (Fig. 7h). In contrast, the OHMs₁₃₀ structure possessed more V_{sh-O} than the OHMs₁₇₀ structure, resulting in the contribution ratio of the pseudo process for OHMs₁₃₀ being larger than that of OHMs₁₇₀ electrode during discharge (Fig. 7h). In addition, the OHMs₁₃₀ electrode revealed a lower capacity than the OHMs₁₇₀ electrode (Fig. 7(a,b)) because of the presence of defects in more of the MoO₄ tetrahedra in OHMs₁₃₀ compared to OHMs₁₇₀. These results indicated that the pseudo phenomenon occurred on the OHM anodes and substantially influenced the entire capacity, resulting in an excellent rate capacity and excellent cycling durability for the electrode.

4. Conclusion

In this work, we demonstrated that the open structure and defect engineering successfully improved the electrochemical performance of alkaline-molybdate-based materials. The 3D channels and layer structure of the OHMs facilitate the movement of Li⁺ ions. Moreover, the oxygen vacancies (i.e., V_O consisting of V_{sh-O} and V_{water-O}) created in the OHMs via the hydrothermal process and heat treatment play important roles under the appropriate reaction conditions. The V_O in the OHMs significantly enhanced electrical conductivity, increased Li⁺ mobility, promoted the pseudo process, and suppressed volume change during lithiation/delithiation processes, which were confirmed by advanced techniques including positron annihilation lifetime measurement. Consequently, the electrode made of the defect-engineered OHMs showed an excellent reversible capacity and longer stability compared to the ordinary OHMs and other alkaline metal molybdates. Additionally, the defect-engineered OHMs were found to be among the rarest materials capable of maintaining high current densities in the rate test. The OHMs developed in this work exhibited promising lithium storage capabilities and excellent stability, making them a viable anode candidate for producing cost-effective and high-performance LIBs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2022.137174>.

References

- [1] X. Zhu, J. Xu, Y. Luo, Q. Fu, G. Liang, L. Luo, Y. Chen, C. Lin, X. Zhao, MoNb₁₂O₃₃ as a new anode material for high-capacity, safe, rapid and durable Li⁺ storage: structural characteristics, electrochemical properties, and working mechanisms, *J. Mater. Chem. A* 7 (2019) 6522–6532, <https://doi.org/10.1039/C9TA00309F>.
- [2] Q. Fu, X. Zhu, R. Li, G. Liang, L. Luo, Y. Chen, Y. Ding, C. Lin, K. Wang, X.S. Zhao, A low-strain V₃Nb₁₇O₅₀ anode compound for superior Li⁺ storage, *Energy Storage Mater.* 30 (2020) 401–411, <https://doi.org/10.1016/j.ensm.2020.05.012>.
- [3] J. Huang, Q. Chen, S. Chen, L. Luo, J. Li, C. Lin, Y. Chen, Al³⁺-doped FeNb₁₁O₂₉ anode materials with enhanced lithium-storage performance, *Adv. Compos. Hybrid Mater.* 4 (2021) 733–742, <https://doi.org/10.1007/s42114-021-00291-4>.
- [4] L. Yang, G. Liang, H. Cao, S. Ma, X. Liu, X. Li, G. Chen, W. You, C. Lin, R. Che, A new sodium calcium cyclotetranadate framework “zero-strain” during large-capacity lithium intercalation, *Adv. Funct. Mater.* 32 (2022) 2105026, <https://doi.org/10.1002/adfm.202105026>.
- [5] S. Ma, T. Jiang, J. Deng, Q. Zhang, Y. Ou, X. Liu, C. Lin, K. Wang, X. Zhao, VPOs: an all-climate lithium-storage material, *Energy Storage Mater.* 46 (2022) 366–373, <https://doi.org/10.1016/j.ensm.2022.01.032>.
- [6] F. Xin, M.S. Whittingham, Challenges and development of tin-based anode with high volumetric capacity for Li-ion batteries, *Electrochem. Energ. Rev.* 3 (2020) 643–655, <https://doi.org/10.1007/s41918-020-00082-3>.
- [7] K. Liu, C. Li, L. Yan, M. Fan, Y. Wu, X. Meng, T. Ma, MOFs and their derivatives as Sn-based anode materials for lithium/sodium ion batteries, *J. Mater. Chem. A* 9 (2021) 27234–27251, <https://doi.org/10.1039/D1TA06996A>.
- [8] C. Sun, M. Liu, L. Wang, L. Xie, W. Zhao, J. Li, S. Liu, D. Yan, Q. Zhao, Revisiting lithium-storage mechanisms of molybdenum disulfide, *Chin. Chem. Lett.* (2021), <https://doi.org/10.1016/j.ccl.2021.08.052>.
- [9] L. Xie, L. Wang, W. Zhao, S. Liu, W. Huang, Q. Zhao, WS₂ moiré superlattices derived from mechanical flexibility for hydrogen evolution reaction, *Nat. Commun.* 12 (2021) 5070, <https://doi.org/10.1038/s41467-021-25381-1>.
- [10] L. Wang, L. Xie, W. Zhao, S. Liu, Q. Zhao, Oxygen-facilitated dynamic active-site generation on strained MoS₂ during photo-catalytic hydrogen evolution, *Chem. Eng. J.* 405 (2021), 127028, <https://doi.org/10.1016/j.cej.2020.127028>.
- [11] C. Liu, C. Wang, X. Meng, X. Li, Q. Qing, X. Wang, R. Xue, Q. Yu, J. Yang, K. Wang, Tungsten nitride nanoparticles anchored on porous borocarbonitride as high-rate anode for lithium ion batteries, *Chem. Eng. J.* 399 (2020), 125705, <https://doi.org/10.1016/j.cej.2020.125705>.
- [12] Z. Li, C. Wang, X. Chen, X. Wang, X. Li, Y. Yamauchi, X. Xu, J. Wang, C. Lin, D. Luo, MoO_x nanoparticles anchored on N-doped porous carbon as Li-ion battery electrode, *Chem. Eng. J.* 381 (2020), 122588, <https://doi.org/10.1016/j.cej.2019.122588>.
- [13] D.E. Polyak, Molybdenum statistics and information, in: *Mineral Commodity Summaries*, U.S. Geological Survey, 2020, pp. 110–111.
- [14] Z.Y. Zhang, W.Y. Li, T.W. Ng, W.P. Kang, C.S. Lee, W.J. Zhang, Iron(II) molybdate (FeMoO₄) nanorods as a high-performance anode for lithium ion batteries: structural and chemical evolution upon cycling, *J. Mater. Chem. A* 3 (2015) 20527–20534, <https://doi.org/10.1039/C5TA05723J>.
- [15] L. Wang, Y.C. He, Y.L. Mu, B. Wu, M.J. Liu, Y. Zhao, X. Lai, J. Bi, D.J. Gao, Sol-Gel Driving LiFe(MoO₄)₂ Microcrystals: High Capacity and Superior Cycling Stability for Anode Material in Lithium Ion Batteries, *Electron. Mater.* 15 (2019) 186–191, <https://doi.org/10.1007/s13391-018-00115-6>.
- [16] J.Y. Zhang, R.L. Li, Q. Chen, G.H. Zhao, J.F. Jia, Porous carbon-coated Li₂MoO₄ as high-performance anode materials for lithium-ion batteries, *Mater. Lett.* 233 (2018) 302–305, <https://doi.org/10.1016/j.matlet.2018.09.032>.
- [17] X.D. Liu, Y.C. Lyu, Z.H. Zhang, H. Li, Y.S. Hu, Z.X. Wang, Y.M. Zhao, Q. Kuang, Y. Z. Dong, Z.Y. Liang, Q.H. Fan, L.Q. Chen, Nanotube Li₂MoO₄: a novel and high-capacity material as a lithium-ion battery anode, *Nanoscale* 6 (2014) 13660–13667, <https://doi.org/10.1039/C4NR04226C>.
- [18] X.D. Liu, Y.M. Zhao, Y.Z. Dong, Q. Kuang, Z.Y. Liang, X.H. Lin, D.L. Yan, H.T. Liu, Synthesis of Carbon-coated Nanoplate alpha-Na₂MoO₄ and its Electrochemical Lithiation Process as Anode Material for Lithium-ion Batteries, *Electrochim. Acta* 154 (2015) 94–101, <https://doi.org/10.1016/j.electacta.2014.12.082>.
- [19] N. Sharma, K.M. Shaju, G.V.S. Rao, B.V.R. Chowdari, Z.L. Dong, T.J. White, Carbon-coated nanophase CaMoO₄ as anode material for Li ion batteries, *Chem. Mater.* 16 (2004) 504–512, <https://doi.org/10.1021/cm0348287>.
- [20] Y.G. Liang, X.Y. Han, Z.H. Yi, W.C. Tang, L.Q. Zhou, J.T. Sun, S.J. Yang, Y.H. Zhou, Synthesis, characterization and lithium-intercalation properties of rod-like CaMoO₄ nanocrystals, *J. Solid. State Electr.* 11 (2007) 1127–1131, <https://doi.org/10.1007/s10008-006-0249-1>.
- [21] Y. Zhang, L. Tao, C. Xie, D. Wang, Y. Zou, R. Chen, Y. Wang, C. Jia, S. Wang, Defect engineering on electrode materials for rechargeable batteries, *Adv. Mater.* 32 (2020) 1905923, <https://doi.org/10.1002/adma.201905923>.
- [22] P. Zeng, Y. Zhao, Y. Lin, X. Wang, J. Li, W. Wang, Z. Fang, Enhancement of electrochemical performance by the oxygen vacancies in hematite as anode

- material for lithium-ion batteries, *Nanoscale Res. Lett.* 12 (2017) 1–9, <https://doi.org/10.1186/s11671-016-1783-0>.
- [23] S. Wang, L. Li, W. He, Y. Shao, Y. Li, Y. Wu, X. Hao, Oxygen Vacancy Modulation of Bimetallic Oxynitride Anodes toward Advanced Li-Ion Capacitors, *Adv. Funct. Mater.* 30 (2020) 2000350, <https://doi.org/10.1002/adfm.202000350>.
- [24] Y. Sun, H. Wang, Q. Xing, W. Cui, J. Li, S. Wu, L. Sun, The pivotal effects of oxygen vacancy on Bi_2MoO_6 : Promoted visible light photocatalytic activity and reaction mechanism, *Chinese, J. Catal.* 40 (2019) 647–655, [https://doi.org/10.1016/S1872-2067\(19\)63277-8](https://doi.org/10.1016/S1872-2067(19)63277-8).
- [25] C. Hou, Y. Hou, Y. Fan, Y. Zhai, Y. Wang, Z. Sun, R. Fan, F. Dang, J. Wang, Oxygen vacancy derived local build-in electric field in mesoporous hollow Co_3O_4 microspheres promotes high-performance Li-ion batteries, *J. Mater. Chem. A* 6 (2018) 6967–6976, <https://doi.org/10.1039/C8TA00975A>.
- [26] N. Li, K. Du, G. Liu, Y. Xie, G. Zhou, J. Zhu, F. Li, H.-M. Cheng, Effects of oxygen vacancies on the electrochemical performance of tin oxide, *J. Mater. Chem. A* 1 (2013) 1536–1539, <https://doi.org/10.1039/C2TA01012G>.
- [27] Y. Zhang, Z. Ding, C.W. Foster, C.E. Banks, X. Qiu, X. Ji, Oxygen vacancies evoked blue TiO_2 (B) nanobelts with efficiency enhancement in sodium storage behaviors, *Adv. Funct. Mater.* 27 (2017) 1700856, <https://doi.org/10.1002/adfm.201700856>.
- [28] Y. Shen, K. Zhang, F. Yang, Z. Li, Z. Cui, R. Zou, Q. Liu, J. Hu, K. Xu, Oxygen vacancies-rich cobalt-doped NiMoO_4 nanosheets for high energy density and stable aqueous Ni-Zn battery, *Sci. China Mater.* 63 (2020) 1205–1215, <https://doi.org/10.1007/s40843-020-1292-6>.
- [29] J. Yang, X. Xiao, P. Chen, K. Zhu, K. Cheng, K. Ye, G. Wang, D. Cao, J. Yan, Creating oxygen-vacancies in MoO_3 -x nanobelts toward high volumetric energy-density asymmetric supercapacitors with long lifespan, *Nano Energy* 58 (2019) 455–465, <https://doi.org/10.1016/j.nanoen.2019.01.071>.
- [30] L. Xu, Q. Jiang, Z. Xiao, X. Li, J. Huo, S. Wang, L. Dai, Plasma-engraved Co_3O_4 nanosheets with oxygen vacancies and high surface area for the oxygen evolution reaction, *Angew. Chem.* 128 (2016) 5363–5367, <https://doi.org/10.1002/ange.201600687>.
- [31] K.V. Kravchik, M.V. Kovalenko, M.I. Bodnarchuk, Colloidal Antimony Sulfide Nanoparticles as a High-Performance Anode Material for Li-ion and Na-ion Batteries, *Sci. Rep.* 10 (2020) 2554, <https://doi.org/10.1038/s41598-020-59512-3>.
- [32] X.C. Hou, G.Y. Zhu, X.Y. Niu, Z.Y. Dai, Z.H. Yin, Q.C. Dong, Y.Z. Zhang, X.C. Dong, Ternary transition metal oxide derived from Prussian blue analogue for high-performance lithium ion battery, *J. Alloy. Compd.* 729 (2017) 518–525, <https://doi.org/10.1016/j.jallcom.2017.09.203>.
- [33] Y. Gogotsi, P. Simon, True performance metrics in electrochemical energy storage, *Science* 334 (2011) 917–918, <https://doi.org/10.1126/science.1213003>.
- [34] M.J. Liu, Q. Wang, Z.Y. Liu, Y. Zhao, X. Lai, J. Bi, D.J. Gao, *In-situ* N-doped MnCO_3 anode material via one-step solvothermal synthesis: Doping mechanisms and enhanced electrochemical performances, *Chem. Eng. J.* 383 (2020), <https://doi.org/10.1016/j.cej.2019.123161>.
- [35] U.T.T. Doan, A.T.T. Pham, T.B. Phan, S. Park, A.T. Luu, Q.H. Nguyen, T.S. Lo, T. D. Tap, M. Ohtani, N.K. Pham, Abnormal volatile and normal stable bipolar resistive switching characteristics of hybrid nanocomposites: Morphology–defects–property Relationship, *J. Alloy. Compd.* 857 (2021), 157602, <https://doi.org/10.1016/j.jallcom.2020.157602>.
- [36] A.T.T. Pham, T.A. Luu, N.K. Pham, H.K.T. Ta, T.H. Nguyen, D. Van Hoang, H.T. Lai, V.C. Tran, J.-H. Park, J.-K. Lee, Multi-scale defects in ZnO thermoelectric ceramic materials co-doped with In and Ga, *Ceram. Int.* 46 (2020) 10748–10758, <https://doi.org/10.1016/j.ceramint.2020.01.084>.
- [37] R. Krause-Rehberg, H.S. Leipner, Positron annihilation in semiconductors: defect studies, (1999).
- [38] J. Kany, Microcomputer program for analysis of positron annihilation lifetime spectra, *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 374 (1996) 235–244, [https://doi.org/10.1016/0168-9002\(96\)00075-7](https://doi.org/10.1016/0168-9002(96)00075-7).
- [39] C.F. Tsang, A. Manthiram, Synthesis of lower-valent molybdenum oxides in aqueous solutions by reducing Na_2MoO_4 with NaBH_4 , *J. Mater. Chem.* 7 (1997) 1003–1006, <https://doi.org/10.1039/A606389F>.
- [40] X. Zhang, W. Sprengel, K. Reichle, K. Blaurock, R. Henes, H.-E. Schaefer, Slow removal of vacancies in $\text{B}_2\text{–Ni}_{52}\text{Al}_{48}$ upon long-term low-temperature annealing, *Phys. Rev. B* 68 (2003), 224102, <https://doi.org/10.1103/PhysRevB.68.224102>.
- [41] J. Stark, Concentration of vacancies in a temperature gradient, *Phys. Rev. B* 21 (1980) 556, <https://doi.org/10.1103/PhysRevB.21.556>.
- [42] V.P.M. Pillai, T. Pradeep, M.J. Bushiri, R.S. Jayasree, V.U. Nayar, Vibrational spectroscopic studies of FeClMoO_4 , Na_2MoO_4 and Na_2MoO_4 center dot $2\text{H}_2\text{O}/\text{D}_2\text{O}$, *Spectrochim. Acta A* 53 (1997) 867–876, [https://doi.org/10.1016/S1386-1425\(96\)01853-7](https://doi.org/10.1016/S1386-1425(96)01853-7).
- [43] A.M. Douvas, M. Vasilopoulou, D.G. Georgiadou, A. Soulati, D. Davazoglou, N. Vourdas, K.P. Giannakopoulos, A.G. Kontos, S. Kennou, P. Argitis, Sol-gel synthesized, low-temperature processed, reduced molybdenum peroxides for organic optoelectronics applications, *J. Mater. Chem. C* 2 (2014) 6290–6300, <https://doi.org/10.1039/C4TC00301B>.
- [44] B.V.R. Reddy, R. Ravikumar, C. Nithya, S. Gopukumar, High performance Na_xCoO_2 as a cathode material for rechargeable sodium batteries, *J. Mater. Chem. A* 3 (2015) 18059–18063, <https://doi.org/10.1039/C5TA03173G>.
- [45] A.A. Bortoti, A. de Freitas Gavanski, Y.R. Velazquez, A. Galli, E.G. de Castro, Facile and low cost oxidative conversion of MoS_2 in $\alpha\text{-MoO}_3$: synthesis, characterization and application, *J. Solid State Chem.* 252 (2017) 111–118, <https://doi.org/10.1016/j.jssc.2017.05.006>.
- [46] Y. Jeong, C. Bae, D. Kim, K. Song, K. Woo, H. Shin, G. Cao, J. Moon, Bias-stress-stable solution-processed oxide thin film transistors, *ACS Appl. Mater. Interfaces* 2 (2010) 611–615, <https://doi.org/10.1021/am900787k>.
- [47] T. Szörényi, L. Laude, I. Bertoti, Z. Kantor, Z. Geretovszky, Excimer laser processing of indium-tin-oxide films: An optical investigation, *J. Appl. Phys.* 78 (1995) 6211–6219, <https://doi.org/10.1063/1.360567>.
- [48] P.-T. Hsieh, Y.-C. Chen, K.-S. Kao, C.-M. Wang, Luminescence mechanism of ZnO thin film investigated by XPS measurement, *Appl. Phys. A* 90 (2008) 317–321, <https://doi.org/10.1007/s00339-007-4275-3>.
- [49] S. Jain, J. Shah, N.S. Negi, C. Sharma, R.K. Kotnala, Significance of interface barrier at electrode of hematite hydroelectric cell for generating ecopower by water splitting, *Int. J. Energy Res.* 43 (2019) 4743–4755, <https://doi.org/10.1002/er.4613>.
- [50] R. Precht, S. Stolz, E. Mankel, T. Mayer, W. Jaegermann, R. Hausbrand, Investigation of sodium insertion into tetracyanoquinodimethane (TCNQ): results for a TCNQ thin film obtained by a surface science approach, *Phys. Chem. Phys.* 18 (2016) 3056–3064, <https://doi.org/10.1039/C5CP06659J>.
- [51] S.W. Tong, H. Medina, W. Liao, J. Wu, W. Wu, J. Chai, M. Yang, A. Abutaha, S. Wang, C. Zhu, Employing a Bifunctional Molybdate Precursor To Grow the Highly Crystalline MoS_2 for High-Performance Field-Effect Transistors, *ACS Appl. Mater. Interfaces* 11 (2019) 14239–14248, <https://doi.org/10.1021/acsami.9b01444>.
- [52] Y.J. Lee, J. Yi, G.F. Gao, H. Koerner, K. Park, J. Wang, K. Luo, R.A. Vaia, J.W. Hsu, Low-temperature solution-processed molybdenum oxide nanoparticle hole transport layers for organic photovoltaic devices, *Adv. Energy Mater.* 2 (2012) 1193–1197, <https://doi.org/10.1002/aenm.201200229>.
- [53] J.-G. Choi, L. Thompson, XPS study of as-prepared and reduced molybdenum oxides, *Appl. Surf. Sci.* 93 (1996) 143–149, [https://doi.org/10.1016/0169-4332\(95\)00317-7](https://doi.org/10.1016/0169-4332(95)00317-7).
- [54] S. Wu, J. Xiong, J. Sun, Z.D. Hood, W. Zeng, Z. Yang, L. Gu, X. Zhang, S.-Z. Yang, Hydroxyl-dependent evolution of oxygen vacancies enables the regeneration of BiOCl photocatalyst, *ACS Appl. Mater. Interfaces* 9 (2017) 16620–16626, <https://doi.org/10.1021/acsami.7b01701>.
- [55] X. YingáKong, Y. YeeáChoo, A. KaháSoh, A. RahmanáMohamed, Oxygen vacancy induced Bi_2WO_6 for the realization of photocatalytic CO_2 reduction over the full solar spectrum: from the UV to the NIR region, *Chem. Commun.* 52 (2016) 14242–14245, <https://doi.org/10.1039/C6CC07750A>.
- [56] Y. Liu, B. Wei, L. Xu, H. Gao, M. Zhang, Generation of oxygen vacancy and OH radicals: a comparative study of Bi_2WO_6 and $\text{Bi}_2\text{WO}_{6-x}$ nanoplates, *Chem. Cat. Chem.* 7 (2015) 4076–4084, <https://doi.org/10.1002/cctc.201500714>.
- [57] C. Zhao, C. Yu, M. Zhang, H. Huang, S. Li, X. Han, Z. Liu, J. Yang, W. Xiao, J. Liang, Ultrafine MoO_2 -Carbon microstructures enable ultralong-life power-type sodium ion storage by enhanced pseudocapacitance, *Adv. Energy Mater.* 7 (2017) 1602880, <https://doi.org/10.1002/aenm.201602880>.
- [58] Z.C. Ju, E. Zhang, Y.L. Zhao, Z. Xing, Q.C. Zhuang, Y.H. Qiang, Y.T. Qian, One-Pot Hydrothermal Synthesis of FeMoO_4 Nanocubes as an Anode Material for Lithium-Ion Batteries with Excellent Electrochemical Performance, *Small* 11 (2015) 4753–4761, <https://doi.org/10.1002/sml.201501294>.
- [59] P. Ge, H. Hou, C.E. Banks, C.W. Foster, S. Li, Y. Zhang, J. He, C. Zhang, X. Ji, Binding MoSe_2 with carbon constrained in carbonous nanosphere towards high-capacity and ultrafast Li/Na-ion storage, *Energy Storage Materials* 12 (2018) 310–323, <https://doi.org/10.1016/j.ensm.2018.02.012>.
- [60] H. Tabassum, R. Zou, A. Mahmood, Z. Liang, Q. Wang, H. Zhang, S. Gao, C. Qu, W. Guo, S. Guo, A universal strategy for hollow metal oxide nanoparticles encapsulated into B/N Co-doped graphitic nanotubes as high-performance lithium-ion battery anodes, *Adv. Mater.* 30 (2018) 1705441, <https://doi.org/10.1002/adma.201705441>.
- [61] X. Pu, D. Zhao, C. Fu, Z. Chen, S. Cao, C. Wang, Y. Cao, Understanding and Calibration of Charge Storage Mechanism in Cyclic Voltammetry Curves, *Angew. Chem.* 133 (2021) 21480–21488, <https://doi.org/10.1002/ange.202104167>.