In Operando X-ray Studies of High-Performance Lithium-Ion Storage in Keplerate-Type Polyoxometalate Anodes

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ABSTRACT: Polyoxometalates (POMs) have emerged as potential anode materials for lithium-ion batteries (LIBs) owing to their ability to transfer multiple electrons. Although POM anode materials exhibit notable results in LIBs, their energy-storage mechanisms have not been well-investigated. Here, we utilize various in operando and ex situ techniques to verify the charge-storage mechanisms of a Keplerate-type POM Na3K3[(MoVI)5MoO7(OH)2·(KSO4)12·(Mo7V30)20H2O·(Mo2V90)·ca200H2O ([Mo72V30]−)] anode in LIBs. The [Mo72V30]− anode provides a high reversible capacity of up to \( \sim 1300 \text{ mA h g}^{-1} \) without capacity fading for up to 100 cycles. The lithium-ion storage mechanism was studied systematically through in operando synchrotron X-ray absorption near-edge structure, ex situ X-ray diffraction, ex situ extended X-ray absorption fine structure, ex situ transmission electron microscopy, in operando synchrotron transmission X-ray microscopy, and in operando Raman spectroscopy. Based on the abovementioned results, we propose that the open hollow-ball structure of the expansion of the microsized materials have been regarded as some of the most promising reactions (Mo6+, an electron/ion sponge that can store a large number of lithium ions and electrons reversibly via multiple and reversible redox reactions, and a semiconductor that allows fast electron transport. Lithium-ion batteries, sodium-ion batteries, and supercapacitors owing to their polynuclear transition-metal oxides, and they have emerged as potential electrode materials for energy-storage devices such as LIBs, sodium-ion batteries, and supercapacitors owing to their superior theoretical capacity (\( \sim 4200 \text{ mA h g}^{-1} \)), the Li–Si alloying process causes a large volume change, which leads to significant performance degradation during cycling. Furthermore, conversion materials exhibit high capacity up to 1000 mA h g\(^{-1}\); however, volume expansion results in severe capacity fading.

KEYWORDS: polyoxometalate, lithium-ion batteries, electrode, anode materials, charge-storage mechanism

1. INTRODUCTION

Lithium-ion batteries (LIBs), which are the most promising energy-storage devices, possess several advantages such as light weight, high energy density (i.e., 150 and 650 W h L\(^{-1}\)), no memory effect, good cycling performance, and low self-discharge rate, which enable their application in portable electronics and electric vehicles. Several anode materials have been explored, and they can be divided into three common types based on the energy-storage mechanisms: (1) intercalation-type (i.e., graphite, \( \text{LiTi}_x\text{O}_{12} \) (LTO), \( \text{TiO}_2 \), \( \text{V}_2\text{O}_5 \), and \( \text{Nb}_2\text{O}_5 \)), (2) alloy-type (i.e., Sn and Sn-based materials), and (3) conversion-type (i.e., \( \text{Fe}_2\text{O}_3 \), \( \text{MnO}_2 \), \( \text{MoO}_3 \), and \( \text{VN} \)). Commercial graphite anodes suffer from low theoretical capacity (\( \sim 372 \text{ mA h g}^{-1} \)), which severely prevents their applications with high energy demands. Other anode materials, such as LTO-based materials, that have excellent cycle stability and high charge–discharge rates conversely exhibit low capacity (\( < 200 \text{ mA h g}^{-1} \)), low electrical conductivity, and gassing issues. Although silicon-based materials have been regarded as some of the most promising anode candidates owing to their superior theoretical capacity (\( \sim 4200 \text{ mA h g}^{-1} \)), the Li–Si alloying process causes a large volume change, which leads to significant performance degradation during cycling. Furthermore, conversion materials exhibit high capacity up to 1000 mA h g\(^{-1}\); however, volume expansion results in severe capacity fading.
composites have been studied as anodes for LIBs, which exhibit high reversible capacities ranging from 286 to 1300 mAh g$^{-1}$.

Among these POM anode materials, Mo-based POMs exhibit superior battery performance. Li et al. reported a composite that combined a Mo-based Anderson-type POM, Na$_2$AlMo$_{10}$O$_{25}$H$_4$ (NAM), with ethylenediamine-functionalyzed reduced graphene oxide (EDAG) as anodes for LIBs.

The NAM–EDAG anode delivered a high reversible capacity of up to 1000 mA h g$^{-1}$ for more than 100 cycles with a high Coulombic efficiency (∼100%) as well as excellent cycling and rate performance. It showed that Mo ions in NAM were reduced to the Mo$^0$ metal phase after discharging to 0 V while they were reoxidized to Mo$^{VI}$ after charging to 3 V by ex situ X-ray photoelectron spectroscopy (XPS) analyses, indicating that NAM can serve as a conversion anode with six electron transfers per Mo ion.

Li et al. proposed that the lithium ions can move between molecular-sized units and increase the conversion efficiency owing to the cluster-like framework of POMs, which leads to a conversion reaction with much higher capacity than MoO$_3$ and with more compact MoO$_6$ linkage.

Song and Streb et al. utilized a sonication-driven strategy to prepare 1D periodically patterned TBA-PMo$_{11}$V/CNT (TBA: CNT: Kepplerate-type hollow-ball structure); Mo$_{72}$V$_{30}$: {Mo$_{72}$V$_{30}$} (Kepplerate-type hollow-ball structure); Mo$_{72}$V$_{30}$: {Mo$_{72}$V$_{30}$} (Kepplerate-type hollow-ball structure); and rGO: reduced graphene oxide (rGO) and studied the effect of the molecular structure on the lithium-ion storage performance. Among these composites, EMi-Mo$_{72}$V$_{30}$@rGO delivers a high reversible capacity of 1145 mAh g$^{-1}$ at 100 mA g$^{-1}$, with an excellent capacity retention (ca. 100% after 500 cycles). It was suspected that the large void space and surface area of the hollow-structured Mo$_{72}$V$_{30}$ might effectively accommodate the lithium ions and buffer the volume expansion; however, the charge-storage mechanism of the key active material Mo$_{72}$V$_{30}$ is not clearly understood or proved and that is fundamentally important and urgently required for further utilization and design of high-performance batteries based on such a high-capacity anode.

Here, in this study, we first reported the lithium-ion storage mechanism of Na$_2$K$_2$3(\{Mo$_{VI}$\}-Mo$_{72}$V$_{30}$O$_{12}$ \{H$_2$O\}$_{30}$ (SO$_4$)$_{0.5}$)}, ca200 H$_2$O, {Mo$_{72}$V$_{30}$}, by various in operando methods. {Mo$_{72}$V$_{30}$} is a Kepplerate-type metal oxide cluster with a diameter of 2.1 nm that is constructed with 12\{Mo$_{VI}$\}-Mo$_{72}$V$_{30}$ pentagonal bipyramids and 30\{V$_{IV}$O$\}$ as linkers, as shown in Figure 1. It has 20 open pore windows on the hollow-ball structure, which is beneficial for lithium-ion transportation. We revealed that a large amount of Mo and V ions with high oxidation states in the {Mo$_{72}$V$_{30}$} molecular cluster allow for multiple redox reactions, leading to its high capacity. The electrochemical properties were carefully studied and the lithium-ion storage mechanism of {Mo$_{72}$V$_{30}$} anodes was clarified with various in operando/ex situ characterization techniques, including in operando synchrotron X-ray absorption near-edge structure (XANES), ex situ X-ray diffraction (XRD), ex situ extended X-ray absorption fine structure (EXAFS), ex situ transmission electron microscopy (TEM), in operando synchrotron transmission X-ray microscopy (TXM), and in operando Raman spectroscopy. The lithium-ion diffusivity was also evaluated via potentiostatic intermittent titration technique (PITT) measurements. These techniques are utilized to study the structural and morphological evolutions, the interfacial change between the electrode and electrolyte, and the dynamic process involved during lithiation/delithiation processes. This work provides insights into the charge-storage mechanism for such complicated POMs through comprehensive analysis techniques, which are important for further studies of POM electrodes in energy-storage applications.

2. EXPERIMENTAL SECTION

2.1. Synthesis of {Mo$_{72}$V$_{30}$}. Na$_2$K$_2$3(\{Mo$_{VI}$\}-Mo$_{72}$V$_{30}$O$_{12}$ \{H$_2$O\}$_{30}$ (SO$_4$)$_{0.5}$)}, ca200 H$_2$O, {Mo$_{72}$V$_{30}$}, was synthesized by a facile solution process as described in the literature.

First, VOSO$_4$·H$_2$O (2.53 g, 10 mmol) was dissolved in 35 mL H$_2$O, and the solution was then added to a conical flask with 8 mL of 0.5 M H$_2$SO$_4$ solution mixed with Na$_2$MoO$_4$·2H$_2$O (2.42 g, 10 mmol). The conical flask with the abovementioned dark purple mixture was sealed using a rubber stopper and stirred at room temperature for 30 min. KCl (0.65 g, 8.72 mmol) was then added to the mixture, which was stirred for another 30 min. The obtained solution was kept in the flask with a rubber stopper for 5 days; purple-black {Mo$_{72}$V$_{30}$} crystals were obtained by filtration. After washing with cold water, the final products were dried under air, and the yield was ∼1 g. Elemental analysis % calcd (found): H 2.6 (2.0); Inductively coupled plasma (ICP) analysis % calcd (found): V 8.55 (8.5), S 2.02 (1.8), Mo 36.0 (36.2), K 4.92 (4.9), Na 0.96 (1); M = 20,009.48 g/mol.

2.2. Material Characterization. A Fourier transform infrared spectroscopy (FT-IR) spectrophotometer (Nicolet Avatar 370) was utilized to detect the infrared spectra of {Mo$_{72}$V$_{30}$}. Na$_2$K$_2$3(\{Mo$_{VI}$\}-Mo$_{72}$V$_{30}$O$_{12}$ \{H$_2$O\}$_{30}$ (SO$_4$)$_{0.5}$)}, ca200 H$_2$O, {Mo$_{72}$V$_{30}$}, was synthesized by a facile solution process as described in the literature. The identity of {Mo$_{72}$V$_{30}$} was also established using the UV–vis spectrum, obtained using a UV–vis spectrophotometer (Varian Cary 5000). The thermogravimetric analysis (TGA) measurement of {Mo$_{72}$V$_{30}$} was recorded using a thermal analyzer (STA 449 F1 Jupiter) under 20 mL min$^{-1}$ flow of argon and the temperature was increased from 25 to 800 °C at a rate of 5 °C min$^{-1}$. The surface morphology of {Mo$_{72}$V$_{30}$} was characterized by field emission SEM (FESEM, Hitachi S8010). The Bruker D2 Phaser X-ray diffractometer was used to characterize the crystal structure of {Mo$_{72}$V$_{30}$} by XRD measurement. Further details on the crystal structure investigation of {Mo$_{72}$V$_{30}$} can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-433790. Elemental analyses were performed using the Elemental Analyserssysteme variop EL III instrument. Raman microscopy (Labram HR800) with a 514

Figure 1. Polyhedral representation for the structure of the Kepplerate-type {Mo$_{72}$V$_{30}$} polyanion.
nm excitation laser was employed to record the Raman spectra of \(\text{Mo}_{72}\text{V}_{30}\). The direct current polarization was measured using a BioLogic potentiostat VMP3 at 3 V within a \(\text{Mo}_{72}\text{V}_{30}\) pellet-coated Pt at the surface. The surface area of \(\text{Mo}_{72}\text{V}_{30}\) was determined by the Brunauer–Emmett–Teller (BET) analysis from the \(\text{N}_2\) adsorption–desorption isotherms obtained at 77 K implemented using the ASAP2020 instrument (Micrometric Corp.).

2.3. Battery Preparation and Characterization. The active layers of anodes were prepared by mixing \(\text{Mo}_{72}\text{V}_{30}\), carbon black (Super P), and sodium carboxymethyl cellulose (CMC) as a binder in DI water with a weight ratio of 70:20:10. Then, it was coated on Cu (Super P), and sodium carboxymethyl cellulose (CMC) as a binder in the BioLogic potentiostat VMP3 at 3 V within a XPS spectrum, and (f) V XPS spectrum of Pt at the surface. The surface area of the anode active material was determined by a facile solution process and characterized with the Brunauer–Emmett–Teller (BET) analysis from the \(\text{N}_2\) adsorption–desorption isotherms obtained at 77 K implemented using the ASAP2020 instrument (Micrometric Corp.).

3. RESULTS

3.1. Material Characterization. \(\{\text{Mo}_{72}\text{V}_{30}\}\) was synthesized by a facile solution process and characterized with the UV–vis spectrum, Raman spectroscopy, single-crystal and powder XRD, TGA, FT-IR, scanning electron microscopy (SEM), and XPS. The vibration peaks of \(\{\text{Mo}_{72}\text{V}_{30}\}\) are presented in the Raman spectrum (\(\lambda: 514 \text{ nm}\)) and the absorption bands observed at 512 \(\text{cm}^{-1}\) and 872 (s, A1gObr)c m

3.2. Cycling Performance. \(\{\text{Mo}_{72}\text{V}_{30}\}\) pellets were prepared and characterized with the Brunauer–Emmett–Teller (BET) analysis from the \(\text{N}_2\) adsorption–desorption isotherms obtained at 77 K implemented using the ASAP2020 instrument (Micrometric Corp.).

3.3. Electrochemical Performance. The XANES data were processed by utilizing the Athena (version 0.9.26) software. The in operando Raman spectroscopy measurements were performed by employing a CR2032 coin cell with quartz windows using a Raman microscope (UniDRON system) with a 530.9 nm excitation laser and 1 mW power. Ex situ TEM was performed using JEOL, JEM-ARM200FTH. In operando TXM was also performed using a CR2032 coin cell with a hole, as mentioned above, at beamline TLS 01B1 at NSRRC in Taiwan. The focused X-rays illuminated the electrode in the coin cell through a capillary condenser. Then, a Fresnel zone plate was used to record high-spatial-resolution transmission X-ray images, which were captured using a CCD camera. After the zone plate, a phase ring was installed at the back focal plane of the zone plate to increase image contrast by optical phase differences. A GCD test was carried out on the in operando cells at a current density of 100 mA g

Figure 2. (a) XRD patterns, (b) TGA spectra, and (c) FT-IR spectra of \(\{\text{Mo}_{72}\text{V}_{30}\}\) before and after drying treatment; (d) FESEM image, (e) Mo XPS spectrum, and (f) V XPS spectrum of \(\{\text{Mo}_{72}\text{V}_{30}\}\) after drying treatment.
before preparing the electrodes for coin cell assembling. The powder XRD pattern of the as-synthesized \{Mo_{72}V_{30}\} is shown in Figure 2a, and the reflections of the as-synthesized \{Mo_{72}V_{30}\} agree with the one simulated from its single-crystal XRD data (CSD-433790, presented in Table S1). The as-synthesized \{Mo_{72}V_{30}\} was heated to 80 °C overnight before preparing the electrodes for coin cell assembling. Almost all reflections for the as-synthesized \{Mo_{72}V_{30}\} after drying at 80 °C overnight disappeared except for the reflections at 11°. This indicates that the long-term crystal structure of \{Mo_{72}V_{30}\} becomes amorphous by removing crystal water after drying, and this phenomenon can also be observed from other POM electrodes in the literature.25,26 Figure 2b displays the TGA data of \{Mo_{72}V_{30}\}. The weight loss below 200 °C is the evaporation of crystal water, and the weight loss after 600 °C indicates the decomposition of \{Mo_{72}V_{30}\}. The amount of crystal water decreases after the drying treatment, as detected by TGA. Figure 2c shows the FT-IR spectrum of the as-synthesized \{Mo_{72}V_{30}\}, which exhibits the characteristic absorption bands: ν = 1618 (m), (δ(H2O)) 1196 (w), 1130 (w), 1055 (w) (υ_{as}(SO_{4}) triplet), 966 (s) (υ(V=O))/υ(Mo=O)), 791 (vs), 633 (w), 575 (s), and 451 (w) (δ(Mo−O−Mo)/υ(Mo−O−Mo)) cm\(^{-1}\), as reported in the literature.25 After the drying treatment, the characteristic absorption bands remain unchanged indicating that the structure of the \{Mo_{72}V_{30}\} polyanion is unchanged. Figure 2d displays the SEM image of \{Mo_{72}V_{30}\} powders that shows irregular shape, and the particle size is around several micrometers. The Mo 3d and V 2p XPS spectrum of \{Mo_{72}V_{30}\} powders is shown in Figure 2e,f. The oxidation states of \{Mo_{72}V_{30}\} after drying treatment are Mo\(^{6+}\) (3d_{3/2} binding energy of 235.6 ± 0.2 eV and 3d_{5/2} of 232.4 ± 0.2 eV) and V\(^{5+}\) (2p_{3/2} binding energy of 516.2 ± 0.2 eV), as reported in the literature.37,38 The direct current polarization test was implemented to estimate the electronic conductivity of \{Mo_{72}V_{30}\} through the Hebb–Wagner polarization method,39 as shown in Figure S1c. The electronic conductivity of \{Mo_{72}V_{30}\} is about 2.65 × 10\(^{-6}\) S cm\(^{-1}\) which is higher than that of the commercial LTO anode (10\(^{-8}\)−10\(^{-13}\) S cm\(^{-1}\)).39,40,41 Figure S1d shows the N\(_2\) adsorption–desorption isotherms for \{Mo_{72}V_{30}\} powder, and the BET surface area is around 0.19 cm\(^{2}\) g\(^{-1}\).

3.2. Electrochemical Characterization. To understand the electrochemical performance of \{Mo_{72}V_{30}\} as an anode material for LIBs, CV and GCD measurements were employed in a half-cell configuration. The half-cells were first lithiated from the open-circuit voltage (OCV) to 0.01 V versus Li/Li\(^+\) and subsequently, they cycled between 0.01 and 3 V versus Li/Li\(^+\). The CV curves of \{Mo_{72}V_{30}\} anodes were carried out at a scan rate of 0.1 mV s\(^{-1}\), as shown in Figure 3a. The higher reduction current in the first cycle of the CV curves as compared to the second cycle in the range of 0.01−0.5 V might be attributed to the formation of solid–electrolyte interphase (SEI) and irreversible insertion.35 The insertion of Li\(^{+}\) into \{Mo_{72}V_{30}\} can be observed in the range of 0.3−1.3 V and at the reduction peak of ~0.01 V versus Li/Li\(^+\). The broad region in the oxidation curve range from 0.75 to 2.0 V versus Li/Li\(^+\) could be contributed from the deinsertion of Li\(^{+}\) from \{Mo_{72}V_{30}\}. The broad potential range for Li\(^{+}\) insertion/extraction in the CV curve can be ascribed to the random distribution of free spaces in the highly disordered structures of \{Mo_{72}V_{30}\} and the continuous redox reactions by the multiple redox centers in one molecule.

Figure 3b displays GCD profiles of \{Mo_{72}V_{30}\} as an anode in a half-cell configuration at a current density of 100 mA g\(^{-1}\) in the 1st, 2nd, and 100th cycles. It shows a steady curve with several obscure plateaus in the potential range between 0.01
and 2.5 V versus Li/Li⁺ indicating the combination of intercalation and capacitive-like storage behaviors with the continuous insertion of Li ions. This results in a high reversible capacity up to ca. 1300 mA h g⁻¹, which is contributed from the multiple redox centers in \{Mo₇₂V₃₀\}. This value is much higher than the commonly used intercalation-type anode materials, for example, graphite (theoretical capacity ≈ 372 mA h g⁻¹) and LTO (100–200 mA h g⁻¹). The lithiation curve of \{Mo₇₂V₃₀\} showed a nonobvious lithiation platform for the first cycle. However, it exhibited an obvious and consistent lithiation platform at 1.25 V in the 2nd and 100th cycle. It was owing to the activation process after the initial few cycles. The Li ion can insert into \{Mo₇₂V₃₀\} molecules more easily after the activation process thus the capacity increased. This activation process can be confirmed by the increase in the Li-ion diffusion coefficient after several cycles, which will be discussed later in the kinetic process analyses. Figure 3c displays the rate performance at different current densities from 100 to 2000 mA g⁻¹. The average specific capacities are approximately 1290, 1273, 1187, 1098, and 979 mA h g⁻¹ at current densities of 100, 200, 500, 1000, and 2000 mA g⁻¹, respectively, suggesting that the \{Mo₇₂V₃₀\} anode can provide good rate performance. The cycling performance of the \{Mo₇₂V₃₀\} anode in LIB at a current density of 100 mA h g⁻¹ is shown in Figure 3d. The first lithiation and delithiation capacities are 1578 and 1292 mA h g⁻¹, respectively, with the Coulombic efficiency of around 81.8%. The first irreversible capacity might be attributed to the formation of SEI. After 100 cycles, the capacity slightly increased from 1292 (the second reversible discharge capacity) to 1495 mA h g⁻¹ with the Coulombic efficiency of about 99.0%, indicating excellent cycling stability and high reversibility. The slightly increased capacity in the initial 50 cycles might be due to an electrochemical activation process that creates the lithium-

Figure 4. (a) Normalized in operando synchrotron Mo K-edge XANES spectra of \{Mo₇₂V₃₀\} measured at different potentials vs Li/Li⁺ at a current density of 100 mA g⁻¹ (blue: the lithiation process; red: the delithiation process). (b) Normalized in operando synchrotron Mo K-edge XANES spectra of \{Mo₇₂V₃₀\} in the first cycle at a potential of OCV (2.86 V), the first full lithiation (1L, 0.01 V), the first full delithiation (1D, 3 V), and the second full lithiation (2L, 0.01 V), compared with MoO₃, MoO₂, and Mo metal foil reference materials. (c) Average Mo valence of \{Mo₇₂V₃₀\} as a function of the potential. (d) Normalized in operando synchrotron V K-edge XANES spectra of \{Mo₇₂V₃₀\}. (e) Normalized in operando synchrotron V K-edge XANES spectra of OCV, 1L, and 1C compared with V₂O₅, VO₂, V₂O₃, and V metal foil. (f) Average V valence of \{Mo₇₂V₃₀\} as a function of the potential.
ion transportation channels in the anode materials.\textsuperscript{44,45} It was quite astonishing to achieve the high capacity, excellent stability, and rate capability for the pristine \{Mo\textsubscript{72}V\textsubscript{30}\}. The reversible capacity of \{Mo\textsubscript{72}V\textsubscript{30}\} (\textasciitilde{}1300 mAh g\textsuperscript{-1} at 100 mA g\textsuperscript{-1}) is approximately three times higher than that of the commercial graphite anode (372 mAh g\textsuperscript{-1}). Compared with other POM anodes,\textsuperscript{22-33} the \{Mo\textsubscript{72}V\textsubscript{30}\} anode conducts much higher capacity and cycling stability, indicating that it is a promising anode material for LIBs.

### 3.3. Charge-Storage Mechanism Studies

Owing to the excellent electrochemical performance and unique features of the \{Mo\textsubscript{72}V\textsubscript{30}\} anode, we conducted several in situ and ex situ techniques to investigate the charge-storage mechanism. Lan et al. utilized ex situ XPS measurement to investigate the oxidation state of Mo and V in EMI-Mo\textsubscript{72}V\textsubscript{30}@rGO before and after being lithiated to 0.01 V, and they found out that the Mo can be reduced from Mo\textsuperscript{6+} to Mo\textsuperscript{4+} and V can be reduced from V\textsuperscript{5+} to V\textsuperscript{2+}. Our ex situ XPS results in Figure S3 also indicate the valence change in Mo and V in \{Mo\textsubscript{72}V\textsubscript{30}\}, where the oxidation states of Mo were partially reduced from Mo\textsuperscript{6+} to Mo\textsuperscript{4+}/Mo\textsuperscript{3+} after being lithiated to 0.01 V versus Li/Li\textsuperscript{+}, and the oxidation states of V were partially reduced from V\textsuperscript{5+}/V\textsuperscript{4+} to V\textsuperscript{3+}/V\textsuperscript{2+} after being lithiated to 0.01 V versus Li/Li\textsuperscript{+}. After being delithiated to 3 V versus Li/Li\textsuperscript{+}, the oxidation states of Mo and V returned back to the initial states (Mo\textsuperscript{6+} and V\textsuperscript{4+}/V\textsuperscript{3+}). However, the ex situ measurement cannot accurately determine the valence number change because it is too sensitive to the ambient air. Therefore, in operando XANES is necessary to determine the exact redox reactions during cycling.

To investigate which oxidation states are involved and how many electrons are transferred during the lithiation/delithiation processes exactly, the in operando synchrotron Mo and V K-edge XANES spectra of \{Mo\textsubscript{72}V\textsubscript{30}\} were employed. Figure 4a displays the Mo K-edge XANES spectra of the \{Mo\textsubscript{72}V\textsubscript{30}\} anode during the first lithiation, the first delithiation, and the second lithiation processes at 100 mA g\textsuperscript{-1}; it reveals a systematic and reversible energy shift. In order to figure out the valence change in Mo ions, MoO\textsubscript{3}, MoO\textsubscript{2} powders, and Mo metal foil were used as references (each of them was calibrated by Mo metal foil), as shown in Figure S4. The XANES spectra for the initial two cycles are shown in Figure 4b with the potentials at OCV (ca. 2.86 V), the first full lithiation at 0.01 V versus Li/Li\textsuperscript{+} (1.1 V), the first full delithiation at 3 V versus Li/Li\textsuperscript{+} (1 D), and the second lithiation at 0.01 V versus Li/Li\textsuperscript{+} (2.1 V). Owing to the low-edge jump, the self-absorption phenomenon is not evident, as observed in Figure 4b. A low-energy shift of the absorption curves during the lithiation process can be observed, and the curve shifts back to the initial position after the delithiation process. The energy edge of OCV is close to that of MoO\textsubscript{3}, indicating that the valence of Mo at OCV is close to Mo\textsuperscript{6+}. When the electrode was lithiated to 0.01 V versus Li/Li\textsuperscript{+}, the energy edge move to a lower energy which is between V metal and V\textsubscript{2}O\textsubscript{3}, indicating that the average valence of vanadium is lower than V\textsuperscript{5+}. Then, the energy edge shifts to higher energy close to V\textsubscript{2}O\textsubscript{5} at the full delithiation state indicating that V is oxidized to higher valence (ca. V\textsuperscript{4+}). Through linear combination fitting, the averaged valence of the vanadium ion in \{Mo\textsubscript{72}V\textsubscript{30}\} at different potentials can be determined, as shown in Figure 4f. Similar to the XPS result, the average valence of the \{Mo\textsubscript{72}V\textsubscript{30}\} electrode at OCV is ca. V\textsuperscript{4+}. The oxidation state of V in the \{Mo\textsubscript{72}V\textsubscript{30}\} electrode before cycling was partially oxidized from V\textsuperscript{4+} to V\textsuperscript{5+}, which may be attributed to the oxidation reaction of \{Mo\textsubscript{72}V\textsubscript{30}\} during the electrode preparation process. During the first lithiation process, the average valence of vanadium decreased to ca. V\textsuperscript{4+}. The valence of V oxidized to V\textsuperscript{5+} after the first full delithiation process. This result indicates that the V ion in one \{Mo\textsubscript{72}V\textsubscript{30}\} molecule can transfer ca. 120 additional electrons (assumed that all the V\textsuperscript{5+} ions in \{Mo\textsubscript{72}V\textsubscript{30}\} are reduced to V\textsuperscript{2+}). Therefore, it demonstrates that the lithiation/delithiation processes of the \{Mo\textsubscript{72}V\textsubscript{30}\} anode are accompanied with several reversible redox reactions from both Mo and V ions in the \{Mo\textsubscript{72}V\textsubscript{30}\} molecule, which leads to high capacity and cycling stability, as shown in Figure 3d.

According to the result obtained from the in operando synchrotron XANES, we proposed the following redox reactions of the \{Mo\textsubscript{72}V\textsubscript{30}\} molecule

\[
\text{Na}_3\text{K}_{23}\{\text{Mo}_{72}\text{V}_{30}\}^V \rightarrow 480\text{Li}^+ + 480\text{e}^-
\]

\[
\leftrightarrow \text{Li}_{480}\text{Na}_3\text{K}_{23}\{\text{Mo}_{72}\text{V}_{30}\}^I
\]

Based on this equation, ca. 480 electrons transfer in one \{Mo\textsubscript{72}V\textsubscript{30}\} molecule, and a theoretical capacity of 754 mAh g\textsuperscript{-1} can be estimated. However, the experimental values exceed the expected value. This is similar to the results reported by Awaga et al. with TBAI\textsubscript{2}[PMo\textsubscript{12}O\textsubscript{40}]@RGO electrodes.\textsuperscript{30} Dunn et al. proposed a theory that the excess capacity is due to the interfacial lithium-storage mechanism, that is, the capacitive behavior, which consists of the non-Faradaic capacity, electrical double-layer capacitance, and pseudocapacitance.\textsuperscript{47} Therefore,
we also simulated the capacitive behavior using Dunn’s method. Figure 5a displays the CV curves measured at different scan rates ranging between 0.1 and 5 mV s\(^{-1}\). The capacities calculated from CV curves at scan rates ranging between 0.1 and 5 mV s\(^{-1}\) are similar to the capacities obtained from GCD with the current densities between 100 and 2000 mA g\(^{-1}\). Therefore, we analyzed the surface-limited capacitive and diffusion-controlled process via CV curves between 0.1 and 5 mV s\(^{-1}\). The CV peak current \(i\) obeys the power-law relationship with scan rate \(v\): 
\[
 i = a v^b 
\]
where \(a\) and \(b\) are adjustable parameters.\(^{48}\) When \(b = 1\), the capacitive current is proportional to the scan rate \(v\), indicating that the reactions are surface-limited processes. When \(b = 0.5\), it means that the reactions are the diffusion-controlled process.\(^{26}\) The adjustable parameter \(b\) can be measured from the slope of the linear plot, as shown in Figure 5b. It is worth noting that the \(b\) value at 0.34, 1.28, and 1.58 V cathodic current and 1.44 and 2.8 V anodic current. (c) Estimation of pseudocapacitive-controlled charge-storage contribution at a 0.1 mV s\(^{-1}\) scan rate. (d) Comparison of the pseudocapacitive-controlled ratio for different scan rates 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 mV s\(^{-1}\).

Ex situ XRD measurements were conducted to observe the change in the crystal structure of the \(\{\text{Mo}_{72}\text{V}_{30}\}\) electrode during the lithiation/delithiation process, as shown in Figure 6. The cell was first lithiated from OCV to 0.01 V versus Li/Li\(^+\) and then delithiated to 3 V versus Li/Li\(^+\) at a current density of 100 mA g\(^{-1}\). After cycling, the two broad peaks at around 11.4

\[
 i(V) = k_1 v + k_2 v^{0.5} \tag{2}
\]

where \(k_1 v\) and \(k_2 v^{0.5}\) correspond to the current contribution from surface-limited capacitive effects and diffusion-controlled process, respectively. Therefore, it is possible to determine the current response resulted from surface-limited capacitive and diffusion-controlled process by determining \(k_1\) and \(k_2\). In Figure 5c, the voltage profile of the capacitive current response is shown by the shaded area in comparison with the total measured current on a typical CV for \(\{\text{Mo}_{72}\text{V}_{30}\}\) at a scan rate of 0.1 mV s\(^{-1}\). The result shows that the capacity of the capacitive-controlled process is approximately 39.0%, which contributed the excess capacity beyond the theoretical capacity estimated by eq 2. Furthermore, with the increase in the scan rate, the effect of capacitive-controlled process enlarges, as shown in Figure 5d. At a scan rate of 5 mV s\(^{-1}\), the role of capacitive contribution further increased to 82.7%. It demonstrates that surface-limited capacitive behavior dominates the charge-storage process, especially at high scan rates which leads to the excellent rate capability. In brief, the observed high capacity in experiments can be well-explained by the contribution from both the multiple valence change in Mo/V and the capacitive contribution.

Ex situ XRD spectra of \(\{\text{Mo}_{72}\text{V}_{30}\}\) electrodes before cycling, after lithiated to 0.01 V vs Li/Li\(^+\), and delithiated to 3 V vs Li/Li\(^+\). View the full ex situ XRD spectra of \(\{\text{Mo}_{72}\text{V}_{30}\}\) electrodes before cycling, after lithiated to 0.01 V vs Li/Li\(^+\), and delithiated to 3 V vs Li/Li\(^+\).
10.0 Å, and one Mo−O bond with a distance of 1.7 Å, two Mo−O bonds with a distance of 2 Å, and one Mo−O bond with a distance of 2.4 Å. Therefore, the coordination numbers at OCV shown in Table S2 are as expected. After the first lithiation process, the intensities of the peaks at 1.2 and 1.9 Å decreased and increased, respectively. This implies that the coordination numbers of the first and second Mo−O bonds decreased and increased, respectively, as shown in Table S2. This result reveals that the lithium ions formed ionic bonds with the oxygen atoms. Thus, the valence of Mo decreased, which caused the Mo−O bond length to increase during the lithiation process. After the first delithiation process, the FT−EXAFS curve and the coordination number returned to the original state (the same as those at OCV). This demonstrates that the molecular structure of \{Mo_{72}V_{30}\} remains stable and the change in the Mo−O bond length is reversible during the lithiation/delithiation process.

The in operando Raman spectra of the \{Mo_{72}V_{30}\} electrode during the first lithiation process are shown in Figure 8. The background profile was recorded with an active-material free electrode, which was coated with carbon black (Super P) and a sodium CMC binder in the electrolyte. In Figure 8a, the characteristic peaks contributed by the carbon black, binder, and electrolyte are indicated by stars (*). The characteristic peaks of \{Mo_{72}V_{30}\} located at approximately 870 and 960 cm\(^{-1}\) are indicated by circles (●). The Raman band of free EC (891 cm\(^{-1}\)) can be observed at the background and OCV electrodes. During the first lithiation process, a notable peak shift from 891 to 902 cm\(^{-1}\) in the voltage range of 0.5−0.01 V (as shown in the orange region in Figure 8a), which corresponds to the process of lithium-ion-coordinated EC, indicating the formation of the SEI layer on the electrode surface. The characteristic peak of \{Mo_{72}V_{30}\} at 870 cm\(^{-1}\) is covered by the EC signal and it is difficult to distinguish. Nevertheless, as shown in the green region in Figure 8b, the characteristic peak of \{Mo_{72}V_{30}\} at 960 cm\(^{-1}\) can still be observed on the electrodes, even after the first lithiation process. This indicates that the molecular structure of...
remains intact after the lithiation process. This result is consistent with the abovementioned ex situ EXAFS analysis.

The morphologies and microstructures of \{Mo\textsubscript{72}V\textsubscript{30}\} were investigated by ex situ TEM to explore the molecular structural transformation of \{Mo\textsubscript{72}V\textsubscript{30}\} during the lithiation/delithiation process. Figure 9a shows the HRTEM image of \{Mo\textsubscript{72}V\textsubscript{30}\} at OCV. The diameter of a single spherical \{Mo\textsubscript{72}V\textsubscript{30}\} molecule is approximately 2.2 nm. The random arrangement and open framework of \{Mo\textsubscript{72}V\textsubscript{30}\} molecules can facilitate electron/ion transport; thus, \{Mo\textsubscript{72}V\textsubscript{30}\} molecules are beneficial for lithium-ion storage. Figure 9b shows the HRTEM image of the \{Mo\textsubscript{72}V\textsubscript{30}\} electrode after the first full lithiation process. The diameter of \{Mo\textsubscript{72}V\textsubscript{30}\} molecules (\(\sim\) 2.5 nm) is slightly larger than that at OCV. However, the volumetric expansion caused by the lithium-ion intercalation is relatively small as compared with other metal oxide anodes (e.g., SnO\textsubscript{2}: \(\sim\)300%;\textsuperscript{52} MoO\textsubscript{3}: 104%;\textsuperscript{53} and V\textsubscript{2}O\textsubscript{5}: 190%).\textsuperscript{54} Figure 9c displays the HRTEM of the \{Mo\textsubscript{72}V\textsubscript{30}\} electrode after the first full delithiation process. The diameter of \{Mo\textsubscript{72}V\textsubscript{30}\} molecules decreases to the original size. This demonstrates that the lithium ions are inserted into the hollow-structured \{Mo\textsubscript{72}V\textsubscript{30}\} molecule but do not undergo extreme volume expansion during the lithiation process.

To gain additional insights into the volume changes of the microscale particles that occur in the \{Mo\textsubscript{72}V\textsubscript{30}\} anode, we conducted in operando synchrotron TXM measurement. Figure 10a shows the first and second GCD curves during TXM measurement, and Figure 10b displays the corresponding TXM images of a single microsized \{Mo\textsubscript{72}V\textsubscript{30}\} particle (but not a single molecule) in the anode at different lithiation/delithiation states. These TXM images display good contrast between the \{Mo\textsubscript{72}V\textsubscript{30}\} particle and the electrode/electrolyte interface because of their different atomic numbers. During the two completed cycles of lithiation/delithiation processes, the volume of the \{Mo\textsubscript{72}V\textsubscript{30}\} particle did not change significantly, which can be attributed to its amorphous characteristics. The lack of the long-range order in the \{Mo\textsubscript{72}V\textsubscript{30}\} particle can be observed in the XRD patterns. This kind of amorphous structure provides a high tolerance to the small volume expansion of each single \{Mo\textsubscript{72}V\textsubscript{30}\} molecule. These results provide the strong evidence for the excellent cycling stability of the \{Mo\textsubscript{72}V\textsubscript{30}\} anode, as shown in Figure 3d.

The lithium-ion diffusion coefficient (\(D_{Li^+}\)) was estimated using the PITT method. This technique characterizes a battery by small voltage steps, and the change in current is recorded. The Li-ion diffusion coefficient (\(D_{Li^+}\)) can be derived by\textsuperscript{55}

\[
D_{Li^+} = \frac{d \ln(I)}{dt} \frac{4L^2}{\pi^2}
\]

where \(I\) is the current, \(t\) is the step time, \(L\) is the diffusion distance which can be calculated by \(L = V_M n_{eq}/S\), \(V_M\) is the molar volume of the electrode materials, \(n_{eq}\) is the number of moles of the electrode materials in the sample, and \(S\) is the cross-sectional area of the electrode sample and electrolyte. This equation is based on Fick’s second law with the
hypothesis of one-dimensional transport and it was derived based on the long-time approximation \((t \gg L^2/D^{\text{diff}})\). Figure S7a shows the \(I-t\) plots during the first lithiation process. It indicates that the current is stable after the holding time of 3600 s. Figure S7b shows the \(\ln(\text{current})-\ln(t)\) plots and the fitting line from 1000 to 3600 s \((t \gg L^2/D^{\text{diff}})\). The slope of the fitting line represents the diffusion coefficient of lithium ions in \(\text{Mo}_72\text{V}_{30}\) for the first and second lithiation and delithiation processes calculated on eq 3, and the value of \(D_{Li}\) ranged between \(10^{-10}\) and \(10^{-11}\) cm\(^2\) s\(^{-1}\). Table 1 compares the \(D_{Li}\) of LIB anode materials measured by PITT.

**Figure S8** shows the Nyquist plots of the \(\text{Mo}_72\text{V}_{30}\) electrode at different cycles. The Nyquist plots of the \(\text{Mo}_72\text{V}_{30}\) electrode at different cycles are shown in Figure S8 and they are composed of a semicircle in the high-frequency domain and a sloping line in the low-frequency domain. The semicircle is contributed by the charge transfer resistance on the electrode/electrolyte interface, and the sloping line is the Warburg domain, which is dominated by the solid-state diffusion of lithium ions in \(\text{Mo}_72\text{V}_{30}\). The Warburg coefficient, \(A_{W}\), is defined as

\[
A_{W} = \frac{\Delta R_{w}/\Delta\omega^{-1/2}}{D_{Li}/\omega^{-1/2}}
\]

cycles. The Nyquist plots of the \(\text{Mo}_72\text{V}_{30}\) electrode at different cycles are shown in Figure S8 and they are composed of a semicircle in the high-frequency domain and a sloping line in the low-frequency domain. The semicircle is contributed by the charge transfer resistance on the electrode/electrolyte interface, and the sloping line is the Warburg domain, which is dominated by the solid-state diffusion of lithium ions in \(\text{Mo}_72\text{V}_{30}\). The Warburg coefficient, \(A_{W}\), is defined as

\[
A_{W} = \frac{\Delta R_{w}/\Delta\omega^{-1/2}}{D_{Li}/\omega^{-1/2}}
\]

where \(R_{w}\) and \(I_{w}\) are the real and imaginary components of the impedance, respectively, and \(\omega\) is the frequency. The time constant for the finite diffusion process can be defined as

\[
\tau = \frac{1}{\sqrt{2} A_{W} Q_{s} dX/dE^{1/2} A_{w}}
\]

where \(Q_{s}\) is the total charge involved in the charge/discharge process and \(dX/dE\) is the derivative of the intercalation isotherm with respect to \(E\). In linear sweep voltammetry, \(Q_{s}(dX/dE) = I_{CV}/v\), where \(I_{CV}\) is the voltammetric current and \(v\) is the scan rate. \(\tau\) can be calculated using \(A_{s}\) and \(I_{CV}\) in the range of the intercalation potentials. Finally, \(D_{Li}\) can be determined as \(D_{Li} = L^2/\tau\), where \(L\) is the diffusion distance mentioned in the PITT analysis, as shown in Figure 11b. \(D_{Li}\) is approximately \(10^{-9}\) to \(10^{-12}\) cm\(^2\) s\(^{-1}\) and it increases from the first cycle to the second cycle owing to the activation process.

\(D_{Li}\) can also be calculated by utilizing the Randles–Sevcik equation at 25 °C

\[
I_{p} = (2.69 \times 10^{5})n^{1/2} C_{0} D^{1/2} A_{w}^{1/2}
\]

where \(I_{p}\) is the peak current density (A), \(n\) is the electron transfer number, \(C_{0}\) is the maximum Li\(^+\) concentration \((3.5 \times 10^{-3} \text{ mol cm}^{-3})\), \(D\) is the diffusion coefficient of the rate-limiting species \((\text{Li}^+, \text{cm}^2 \text{ s}^{-1})\), \(A\) is the apparent surface area \((\text{cm}^2)\), and \(v\) is the scan rate \((\text{V s}^{-1})\). Figure S9 shows the \(I-v^{1/2}\) plot and its fitting line. The slope of the fitting line can be calculated using \((2.69 \times 10^{5})^{1/2} C_{0} D^{1/2} A_{w}\) in eq 6. The \(D_{Li}\) of \(\text{Mo}_72\text{V}_{30}\) obtained via eq 6 is shown in Figure 11c, and the value ranges from \(10^{-10}\) to \(10^{-12}\) cm\(^2\) s\(^{-1}\), which is similar to the values obtained through the PITT and EIS methods. This proves that the \(D_{Li}\) value of the \(\text{Mo}_72\text{V}_{30}\) anode obtained in this study is reliable.

**4. DISCUSSION**

The \(\text{Mo}_72\text{V}_{30}\) anode exhibits excellent cycling stability, high rate capability, and a high lithium-ion diffusion coefficient \((10^{-9} \text{ to } 10^{-10} \text{ cm}^2 \text{ s}^{-1})\). This is different from conventional...
These features revealed that in operando the rate capability in a current density range of 100 cycle stability of up to 100 cycles without fading, and a high excellent cycling stability. Furthermore, the molecular structure of the single molecule remains, amorphous during the lithiation/delithiation processes. However, the entire microsized particle does not undergo significant volume expansion. This indicates that the absence of the long-range order of the amorphous \{Mo\textsubscript{72}V\textsubscript{30}\} anode results in high tolerability for the volume expansion of the anode during the lithiation/delithiation processes. Additionally, no significant volume expansion of the microsized \{Mo\textsubscript{72}V\textsubscript{30}\} particle can be observed during the lithiation process. This is due to the unique molecular structure and amorphous nature, which result in remarkable cycling stability. These experimental analyses pave the way for the further utilization of the Keplerate-type POM anodes in energy-storage applications.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c09344.

Crystal data; Raman, UV—vis, and XPS spectra of \{Mo\textsubscript{72}V\textsubscript{30}\}; EXAFS model analysis; and calculations detail of \(D_{Li}\) (PDF)

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Funding

This work was financially supported by the Young Scholar Fellowship Program by the Ministry of Science and Technology (MOST) in Taiwan (MOST109-2636-E-007-007) and National Tsing Hua University (109Q2708E1). U. K. acknowledges the German Science Foundation (DFG KO-2288/20-1) and Jacobs University for research support.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the Instrumentation Center at National Tsing Hua University for providing assistance in electron spectroscopy for chemical analysis, XRD measurement for structural analysis, and TEM for morphological and microstructural analyses. The authors also thank Dr. Chih-Wen Pao and Dr. Jeng-Lung Chen for their help on the in operando synchrotron XAS (beamline TPS 44A1) in National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan.

ABBREVIATIONS

\[
\text{M}_{1-x} \cdot \text{V}_{x} \cdot \text{O}_{3} \cdot \text{H}_{2} \cdot \text{O}
\]

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