

TRANSITION METAL-BASED NANOMATERIALS



Molybdenum oxide nanoporous asymmetric membranes for high-capacity lithium ion battery anode

Emilee Larson^{1,b)}, Logan Williams^{1,b)}, Congrui Jin², Xiaobo Chen³, Jake DiCesare¹, Olivia Shepperd¹, Shaowen Xu⁴, Ji Wu^{1,a)} 

¹Department of Chemistry and Biochemistry, Georgia Southern University, 250 Forest Drive, Statesboro, GA 30460, USA

²Department of Civil and Environmental Engineering, University of Nebraska-Lincoln, 362Q Whittier, 2200 Vine St., Lincoln, NE 68583, USA

³Materials Science and Engineering Program, Binghamton University, New York, NY 13902, USA

⁴Department of Mechanical Engineering, Georgia Southern University, 1100 Statesboro Pl Cir, Statesboro, GA 30460, USA

^{a)}Address all correspondence to this author. e-mail: jwu@georgiasouthern.edu

^{b)}These authors contributed equally to this work.

Received: 15 July 2021; accepted: 9 August 2021

The cycling performance of high-capacity lithium ion battery anodes can be significantly improved by adopting 3D nanoporous structures that can efficiently accommodate large volume changes during lithiation and de-lithiation. In this study, various molybdenum oxide nanoporous asymmetric membranes were fabricated on a large scale via a spontaneous non-solvent-induced phase separation process. We explored the effects of polymer precursor, membrane geometry, and annealing condition on the porosity, composition, and electrochemical properties of the membranes as lithium ion battery anodes. We demonstrate that 97% initial capacity of MoO₂ planar asymmetric membrane electrode can be retained in 165 cycles at 120 mA g⁻¹. 74% initial capacity can be maintained while the current density is increased from 60 to 480 mA g⁻¹. This efficient and scalable process to prepare molybdenum oxide-based LIB anode provides another alternative to enhance the electrochemical performance of transition metal oxide anodes at a relatively low fabrication cost.

Introduction

Transition metal oxides like MoO₂, MoO₃, and WO₃ have potential applications as high-capacity materials for lithium ion battery (LIB) anode [1–6]. However, these materials suffer from poor electrical conductivity, sluggish ion diffusivity, non-reversible phase change, and large volume variation during lithiation and de-lithiation, thus leading to inferior electrochemical performance [7–9]. Previously, α -MoO₃ and *m*-MoO₂ nanomaterials embedded in conductive carbon matrix have been adopted to fully utilize their high theoretical capacities (1117 and 838 mAh g⁻¹, respectively vs. 372 mAh g⁻¹ of commercial graphite anode) and improve their electrochemical performance since molybdenum oxide nanomaterials alone don't exhibit premium cyclability [10–12]. The strategy seems to be effective to a certain degree, but extravagant fabrication cost, unsatisfying scalability, and cyclability remain to be addressed. Notably, monoclinic *m*-MoO₂ has semimetal properties with a resistivity of 2×10^{-4}

$\Omega \cdot \text{cm}$ at room temperature, whereas orthorhombic α -MoO₃ is a wide bandgap semiconductor of 3.2 eV, implying that *m*-MoO₂ electrode may demonstrate better rate performance as compared to α -MoO₃, although the theoretical capacity of *m*-MoO₂ is relatively lower [13]. Polymeric asymmetric membranes including reverse osmosis and ultrafiltration membranes have been commercialized for water purification and desalination since 1970s, which can be produced on a large scale using a roll-to-roll technology to provide billions of gallons of drinking water worldwide annually [14–16]. As inspired by the polymeric membrane technology, our laboratory has synthesized various inorganic asymmetric membranes using a non-solvent-induced phase separation process (NIPS) or the so-called phase inversion method to improve the electrochemical performance of various alloying anode materials for high-capacity LIBs and sodium ion batteries (SIBs), such as Si, Ge, Sn, and SnO₂ [17–20]. The inorganic membranes consist of a thin layer of nanopores on top of a

thick layer of macropores, in which the active materials are coated with a very thin film of carbon [21, 22]. The unique asymmetric membrane structure can provide strong mechanical support and void space to accommodate large volume changes during repeated charge/discharge, while the presence of carbon coating can enhance the membrane conductivity and benefit the formation of a relatively stable artificial solid electrolyte interphase (SEI) [17, 19].

In this study, fibrous and planar asymmetric membranes containing MoO_2 and MoO_3 transition metal oxide nanoparticles (NPs) are fabricated and characterized using X-ray spectroscopies, electron microscopes, and thermogravimetric and surface area analyzers to reveal their composition, morphology, and structure as well. Their electrochemical properties as LIB anode are evaluated by using rate and cycling tests, cyclic voltammetry, and electrochemical impedance spectroscopy. Planar MoO_2 asymmetric membrane made from polysulfone precursor and carbonized at 500 °C demonstrates the most outstanding cyclability and rate performance, e.g., > 97% of initial capacity is retained in 165 cycles at 120 mA g^{-1} .

Results and discussion

Fabrication of molybdenum oxide asymmetric membranes

The fabrication of molybdenum oxide asymmetric membranes consists of two major steps (Fig. 1): Firstly, $\alpha\text{-MoO}_3$ (orthorhombic) nanoparticles were synthesized by thermally decomposing ammonium molybdate tetrahydrate in air at 350 °C for 12 h [23]. Secondly, as-synthesized $\alpha\text{-MoO}_3$ nanoparticles were mixed thoroughly with CB, polymer (PS or PAN), and NMP to obtain a uniform slurry, and the slurry was then coated into a thin film that was immersed into DI water to form a planar asymmetric membrane. To produce a fibrous asymmetric membrane, the same slurry was extruded through a 31G needle into DI water using an arbor press to overcome the high viscosity. During the phase inversion process, solvent (NMP) was de-mixed from the polymer and mixed with non-solvent (DI water), leading to the precipitation of polymer, CB, and MoO_3 , and the spontaneous formation of an asymmetric porous structure. CB was used as an additive to enhance the membrane conductivity and as a filler to maintain the porous structure after being carbonized. The polymeric asymmetric membranes were then carbonized to produce inorganic PS/ MoO_2 asymmetric membranes that are electrically conductive and thus suitable for LIB anode. It is believed that carbon can reduce MoO_3 to yield MoO_2 during the high-temperature carbonization as shown below [6]:

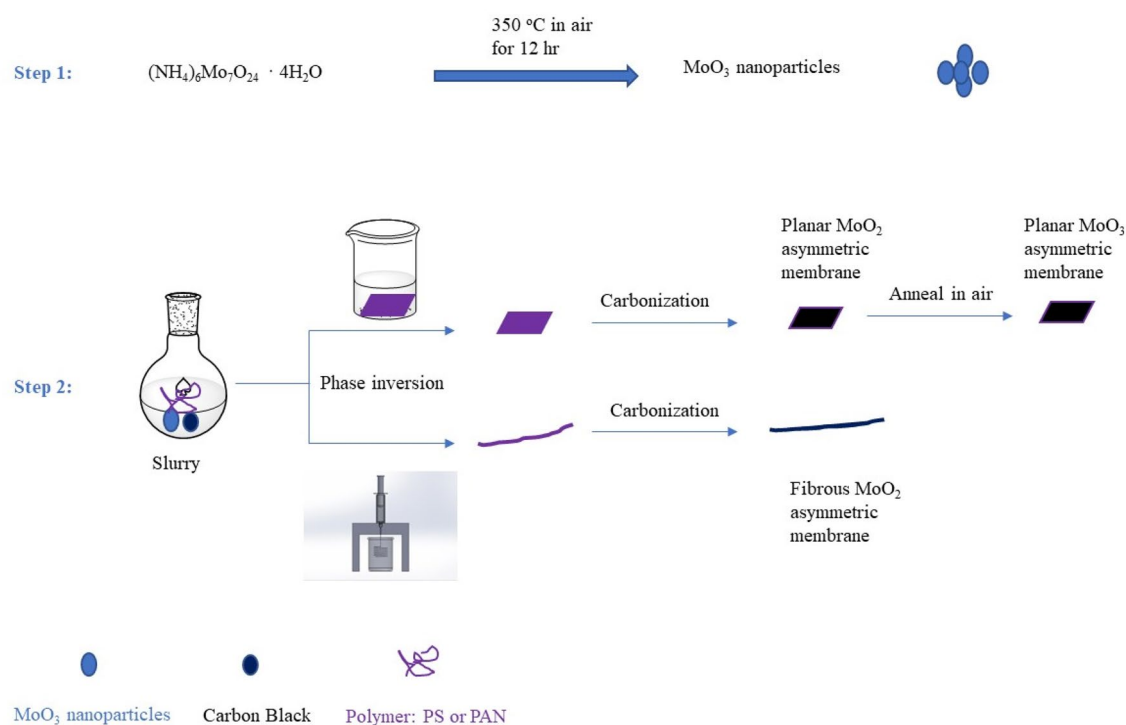
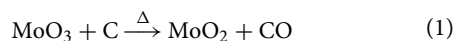


Figure 1: Illustrative diagram showing the fabrication process to obtain asymmetric membranes containing molybdenum oxide nanoparticles for high-capacity lithium ion battery anode.



PS/MoO₂ asymmetric membrane must be annealed in air to obtain PS/MoO₃ asymmetric membrane [11]. However, thermal anneal in air can oxidize CB into CO₂ and thereby affect the contact between the active materials and carbon matrix, which will be discussed later. It is interesting to find out MoO₃ was converted to α-Mo₂C when the asymmetric membrane made from PAN and MoO₃ NPs was carbonized at 800 °C as verified by following PXRD data. It is also notable that the capacity of α-Mo₂C as LIB anode is negligible, although its electrical conductivity is excellent [24]. Recall that PAN must be treated at 800 °C or higher to realize a full carbonization [25]. Molybdenum carbide can be converted to MoO₃ after being thermally annealed in air (PAN/MoO₃ planar asymmetric membrane).

Characterization of molybdenum oxide asymmetric membranes

Figure 2 shows the SEM images of planar and fibrous PS/MoO₂, planar PS/MoO₃ and PAN/MoO₃ membranes, and SEM and TEM images of as-synthesized MoO₃ NPs. It is revealed that the top surface of planar PS/MoO₂ membrane is nanoporous, whereas the bottom surface is macroporous as evidenced in Fig. 2a and S1. In comparison, the surface of fibrous PS/MoO₂ membrane is completely nanoporous, which may hinder the diffusion of lithium ions and thereby reduce the electrode capacity, especially at higher current densities (Fig. 2b and S1). It is also unveiled that the porosity of asymmetric membranes made from PS is higher than that of the membranes made from PAN (Fig. 2c, 2d and S1). This fact is consistent with the literature reports as the type of polymers can affect the thermodynamics and kinetics of the phase inversion process, leading to the formation of membranes with different porosities and pore sizes [26–29]. The porosity of PS/MoO₃ is much higher than PS/MoO₂ membrane because of the partial removal of carbon black during the thermal annealing process as confirmed by the following TGA data (Fig. 2c). Although a higher porosity is generally beneficial to the cycling stability of high-capacity LIB anodes, the removal of nanoscale conductive additives, CB, is detrimental to the contact between the active materials and the conductive carbon matrix when the electrode volume change is large. The size of nanopores on the top surface of asymmetric membranes needs to be further optimized by varying experimental conditions such as phase inversion temperature to reduce lithium ion diffusion barriers while maintaining an excellent cyclability.

Asymmetric membranes were also characterized using TEM and HRTEM for structural and compositional characterizations

(Fig. 3). MoO₂ NPs were found to be uniformly embedded in the carbonaceous matrix of planar and fibrous PS/MoO₂ asymmetric membranes as supported by HRTEM, HAADF imaging, and elemental mapping (Fig. 3a, 3c and S5). The lattice fringes with a d-spacing of 0.343 nm correspond to the (110) facet of monoclinic MoO₂ (Fig. 3b and 3d) [30]. TEM images also show that MoO₃ NPs in planar PS/MoO₃ and PAN/MoO₃ asymmetric membranes aren't in good contact with the carbon matrix as compared to PS/MoO₂ membranes because of the partial loss of carbon during the thermal anneal in air (Fig. 3e and 3g). Lattice fringes with d-spacings of 0.327 and 0.347 nm in planar PS/MoO₃ and PAN/MoO₃ asymmetric membranes are derived from (021) and (040) facets of α-MoO₃, respectively (Fig. 3f and 3h) [31, 32]. Powder X-ray diffraction (PXRD) patterns of as-synthesized MoO₃ NPs match well with those of crystalline orthorhombic α-MoO₃ (Fig. 4 and JCPDS No. 05-0508) [33, 34]. Crystalline monoclinic *m*-MoO₂ was found in the asymmetric membranes carbonized at 500 °C, due to the reduction of α-MoO₃ by carbon at elevated temperatures and under the protection of inert gas, also being consistent with the HRTEM data (Fig. 4 and JCPDS NO. 32-671) [35, 36]. When carbonized at an elevated temperature, e.g., 800 °C, crystalline α-Mo₂C was formed as evident by S4. After being thermally treated in air, *m*-MoO₂ is converted back to α-MoO₃ (Fig. 4). Overall, the PXRD patterns of all membranes and MoO₃ particles are much broader than those of two references due to nanosize and instrumental effects [37]. XPS spectra of MoO₃ NPs, PS/MoO₃, and PAN/MoO₃ membranes have two characteristic peaks at 233.38 and 236.58 eV, which can be satisfyingly attributed to Mo (VI) 3d_{3/2} and 3d_{5/2}, respectively (Fig. 5). Planar PS/MoO₂ membrane has two broad peaks at 232.08 and 228.98 eV, which can be assigned to Mo (IV) 3d_{3/2} and 3d_{5/2} [6]. The binding energies of Mo (IV) 3d_{3/2} and 3d_{5/2} in fibrous PS/MoO₂ membrane are slightly shifted toward higher values, 233.08 and 229.98 eV, which may be due to the complex interplay of screened and unscreened final states or the existence of mixed oxidation states on the top surface [38–40]. The concentrations of MoO₂ and MoO₃ in various asymmetric membranes were determined using a thermogravimetric analyzer (TGA) that used compressed air to burn off carbon and converted MoO₂ to MoO₃ (Table 1). The concentrations of MoO₂ in planar and fibrous PS/MoO₂ membranes are 52.2 and 42.4 wt%, respectively (S2). In contrast, the concentrations of MoO₃ in PS/MoO₃ and PAN/MoO₃ membranes are much higher, i.e., 72.8 and 86.8 wt%, respectively, due to the partial loss of amorphous carbon after being thermally treated in air at 380 °C for 30 min. Notably, pure MoO₃ NPs have a negligible mass change during the TGA analysis (S2). Specific surface areas of various molybdenum oxide asymmetric membranes and MoO₃ NPs are listed in Table 2 and S3. The specific surface area of α-MoO₃ NPs is only 3.66 m² g^{−1}, probably due to the

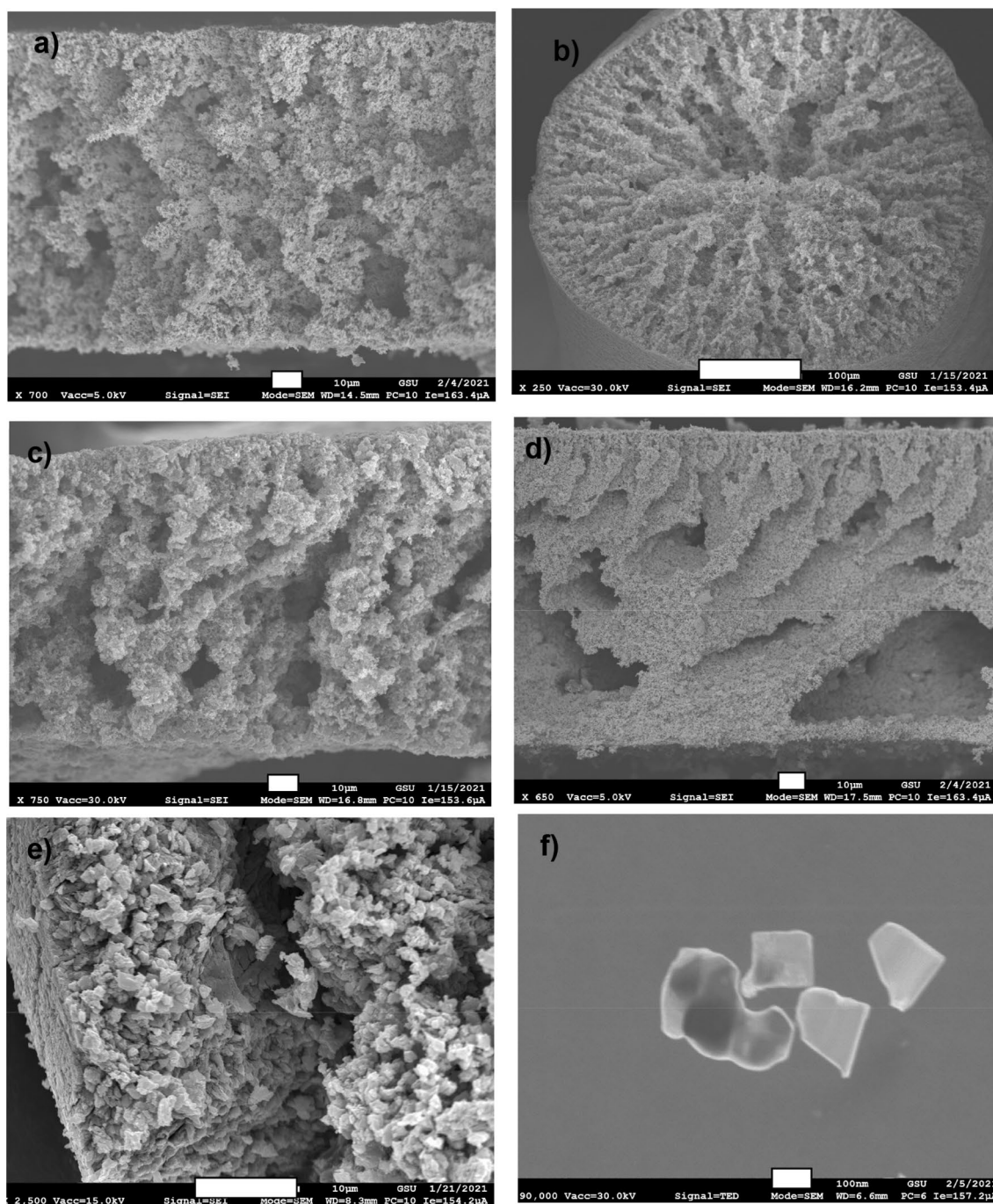
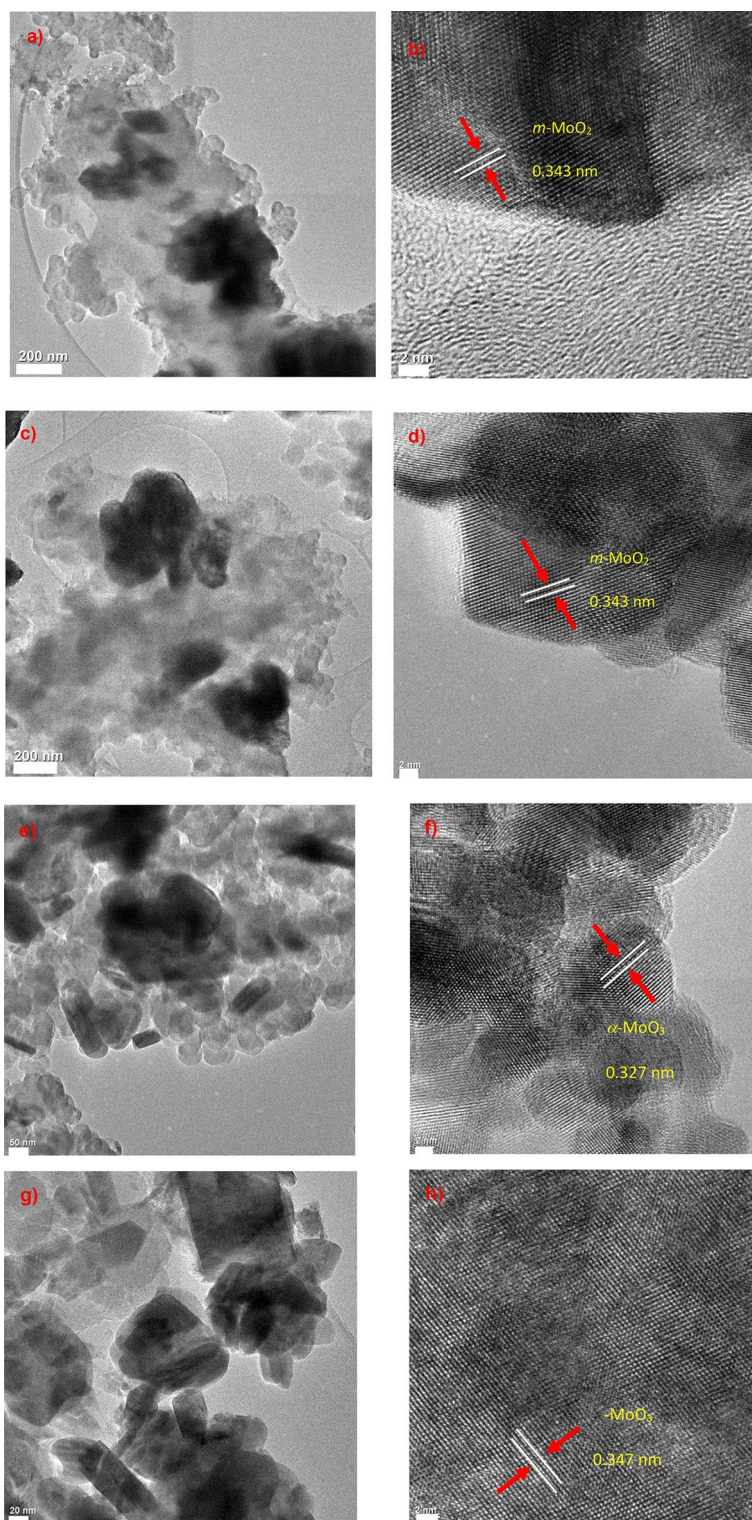


Figure 2: Scanning electron microscope images of (a) PS/MoO₂ planar asymmetric membrane; (b) PS/MoO₂ fibrous asymmetric membrane; (c) PS/MoO₃ planar asymmetric membrane; (d) PAN/MoO₃ planar asymmetric membrane; (e) as-synthesized MoO₃ NPs; and (f) transmission electron microscope image of as-synthesized MoO₃ NPs. Note: scale bars in (a), (c), (d), and (e) are 10 μ m; scale bars in (b) and (f) are 100 μ m and 100 nm, respectively.

stacking and agglomeration of nanoplatelets with flat surfaces as indicated in Fig. 2e and S1. In stark contrast, the surface areas of planar and fibrous PS/MoO₂ membranes are as high as 244 and 140 m² g⁻¹, respectively, thereby benefiting a cycling longevity

since a large number of nanopores may efficiently accommodate large volume changes of MoO₂ NPs during repeated lithiation and de-lithiation. The surface areas of PS/MoO₃ and PAN/MoO₃ membranes that were annealed in air are significantly reduced,

Figure 3: Transmission electron microscope images of (a–b) PS/MoO₂ planar asymmetric membrane; (c–d) PS/MoO₂ fibrous asymmetric membrane; (e–f) PS/MoO₃ planar asymmetric membrane; and (g–h) PAN/MoO₃ asymmetric membrane at different magnifications. Note: scale bars in (b), (d), (f), and (h) HRTEM images are 2 nm; scale bars in (a) and (c) low-resolution TEM images are 200 nm; scale bars in (e) and (g) are 50 and 20 nm, respectively.



e.g., ~28 and 18 m² g⁻¹, respectively. Lower specific surface areas may be linked to the loss of nanoscale carbon black which have a very large specific surface area (45 m² g⁻¹) and function as a filler to prevent the collapses of nanopores.

Electrochemical evaluations of molybdenum oxide asymmetric membranes as LIB anode

PS/MoO₂ planar asymmetric membrane exhibits the most outstanding cyclability as evident by 97.3% capacity retention in

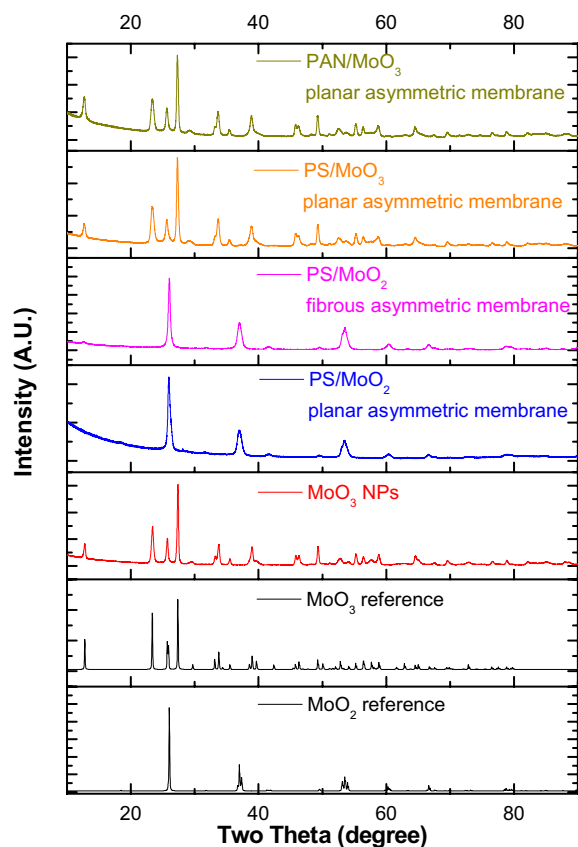


Figure 4: Powder X-ray diffraction patterns of PS/MoO₂ planar asymmetric membrane, PS/MoO₂ fibrous asymmetric membrane, PS/MoO₃ planar asymmetric membrane, PAN/MoO₃ planar asymmetric membrane, and MoO₃ NPs. Note: *m*-MoO₂ and α -MoO₃ reference patterns are also provided for convenient comparison.

165 cycles within a voltage window of 0.01–3.00 V (Fig. 6a). Additionally, the average coulombic efficiency (CE) was calculated to be 99.5% during the whole cycling test. When the current density is increased from 60 to 480 mA g⁻¹, the capacity is only decreased by ~28% (Fig. 6b). Noteworthy, the capacities shown in Fig. 6 were calculated using the total mass of carbon and molybdenum oxide. Assuming the specific capacity of amorphous carbon is ~200 mAh g⁻¹, the specific capacities of MoO₂ in PS/MoO₂ planar asymmetric membrane were estimated to be ~835 and 700 mAh g⁻¹, respectively, at 30 and 60 mA g⁻¹ based on the TGA data (Fig. 6b and Table 1), which is very close to the theoretical capacity of *m*-MoO₂, 838 mAh g⁻¹ [17, 41]. The initial capacity loss (ICL) of PS/MoO₂ planar asymmetric membrane as LIB anode was calculated to be 33.9% as shown in S6. The large ICL can be attributed to the formation of SEI layer and the presence of large amount of nanoscale carbon black that can catalyze irreversible decomposition of electrolyte as reported in the literature [41]. The voltage profiles of PS/MoO₂ planar asymmetric membrane anode at 1st and 150th cycles are almost overlapping with

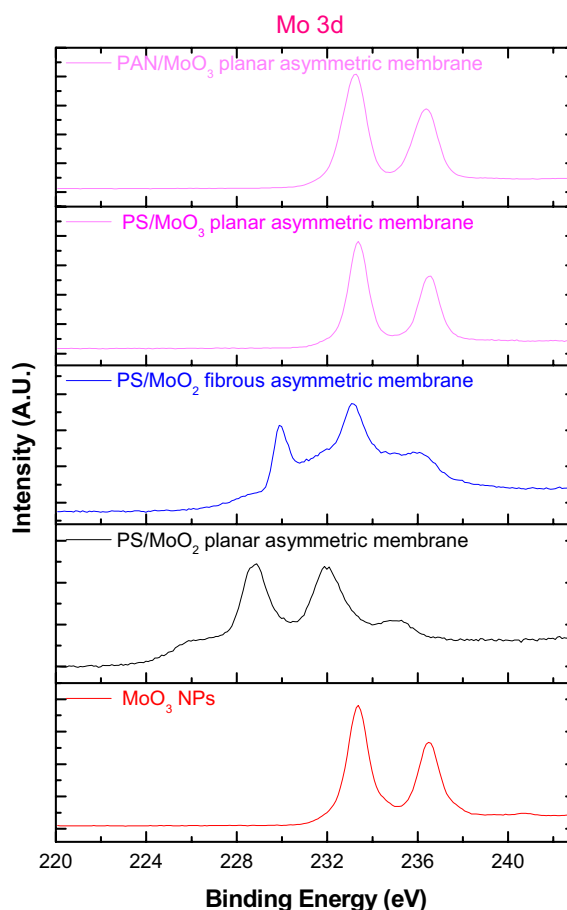


Figure 5: Mo 3d X-ray photoelectron spectra of PS/MoO₂ planar asymmetric membrane, PS/MoO₂ fibrous asymmetric membrane, PS/MoO₃ planar asymmetric membrane, PAN/MoO₃ planar asymmetric membrane, and MoO₃ NPs as well.

TABLE 1: Concentration of MoO₂/MoO₃ and carbon in various types of molybdenum oxide asymmetric membranes as determined by thermogravimetric analyses.

	PS/MoO ₂ planar asymmetric membrane	PS/MoO ₂ fibrous asymmetric membrane	PS/MoO ₃ planar asymmetric membrane	PAN/MoO ₃ planar asymmetric membrane
MoO ₂ wt. %	52.2	42.4	–	–
MoO ₃ wt. %	–	–	72.8	86.8
C wt. %	47.8	57.6	27.2	13.2

each other (Fig. 6d), indicating the electrode has an excellent cycling stability because the asymmetric porous structure can efficiently accommodate the large volume variation and the thin carbon coating is beneficial to the formation of relatively stable artificial SEI layer [19, 42]. It is interesting to find out the electrode has experienced a capacity increase during the first 30 cycles (Fig. 6c). The same phenomenon was previously observed by many other research groups in

TABLE 2: BET (Brunauer, Emmett and Teller) specific surface areas of various molybdenum oxide asymmetric membranes and MoO₃ NPs.

	PS/MoO ₂ planar asymmetric membrane	PS/MoO ₂ fibrous asymmetric membrane	PS/MoO ₃ planar asymmetric membrane	PAN/MoO ₃ planar asymmetric membrane	MoO ₃ NPs
Specific area (m ² g ⁻¹)	243.59 ± 7.24	140.05 ± 3.91	28.14 ± 0.05	18.40 ± 0.05	3.66 ± 0.03

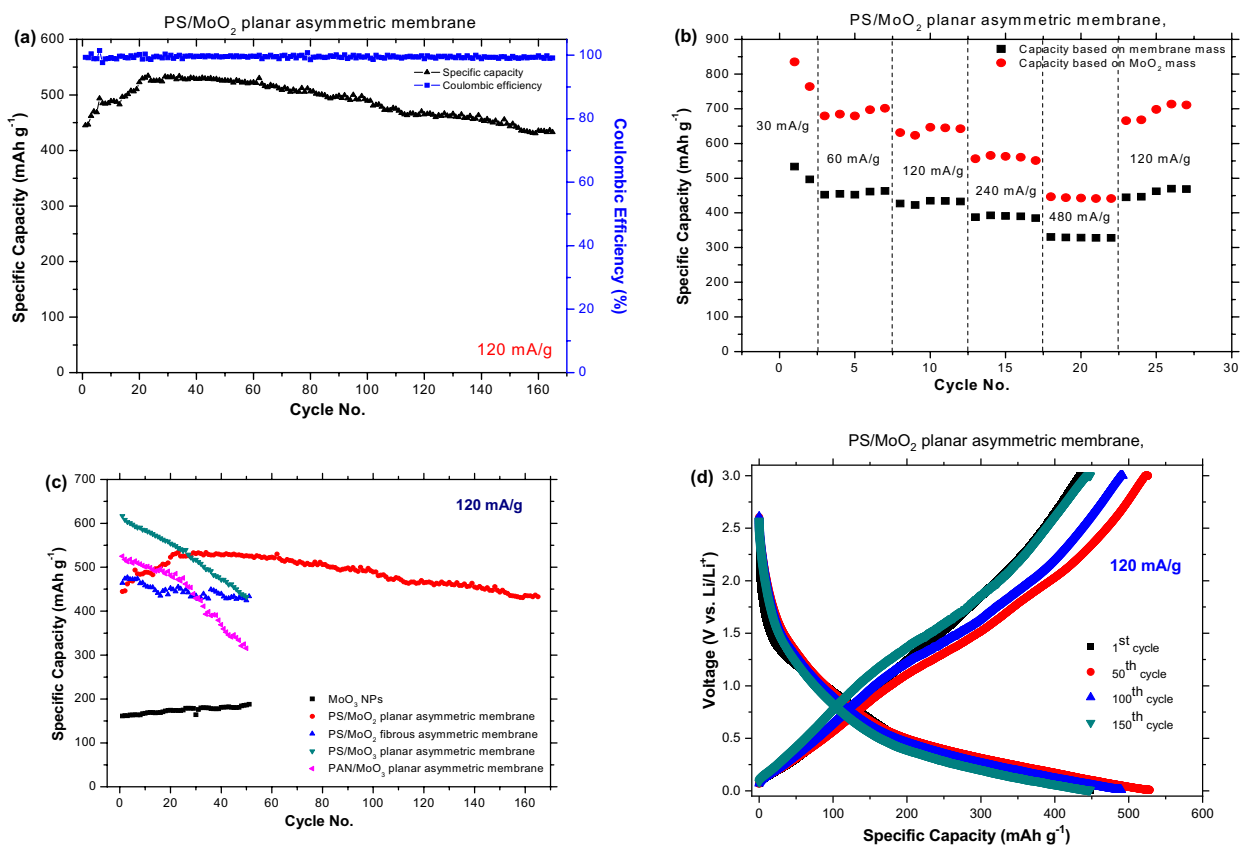


Figure 6: Electrochemical evaluations of molybdenum oxide asymmetric membranes: (a) cycling test and (b) rate performance of PS/MoO₂ planar asymmetric membrane; (c) cycling stability of different types of membranes and MoO₃ NPs; and (d) voltage profiles of PS/MoO₂ planar asymmetric membrane at different cycles.

high-capacity LIB anodes with small lithium ion diffusivities, such as Si and MoO₂ [6, 43, 44]. The underlying reason might be related to the fracture of large nanoparticles into smaller ones out of large volume changes, thereby increasing the materials accessibility and overall capacity, provided that the electrode structure remains integral. Like planar asymmetric membrane, PS/MoO₂ fibrous asymmetric membrane also demonstrates an excellent cyclability as shown in Fig. 6c. However, its overall capacity is lower than the planar counterpart since its surface consists of nanopores only, which may hinder lithium ion diffusion and thus reduce the capacity at the same current density. Both PS/MoO₃ and PAN/MoO₃ planar asymmetric membranes are characterized by initially high capacities (Fig. 6c) because the concentrations of active materials, MoO₃, are very high in the membranes due to the

oxidation of amorphous carbon during the thermal anneal in air. However, the initial capacities are dropped by ~40% in only 50 cycles because the membranes experience much larger volume changes during lithiation and de-lithiation, and the loss of conductive additives, CB, may also do a disservice to the cycling. Most capacity of the control sample, MoO₃ NPs, was lost during the formation cycles, probably due to electrode delamination, fracturing and pulverization [45]. As a result, the capacity is smaller than 200 mAh g⁻¹ in the cycling test, which is close to that of amorphous carbon, although the cycling stability is quite impressive.

Cyclic voltammetry was also employed to study the lithiation/de-lithiation behaviors of PS/MoO₂ planar asymmetric membrane as LIB anode (Fig. 7a). Open circuit potential was scanned between 0.01 and 3.00 V at 0.1, 0.2, 0.4, 0.8, and 1.6 mV/s in

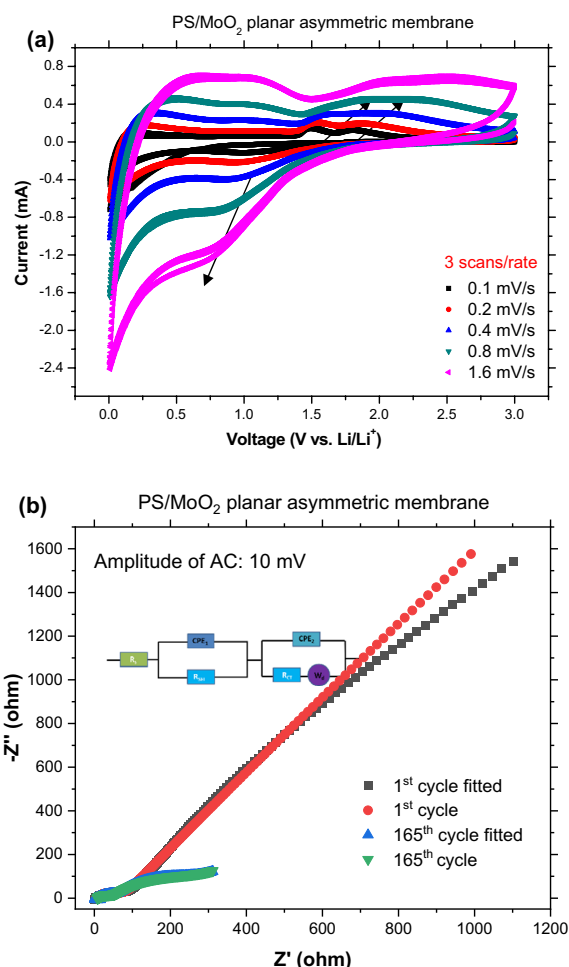


Figure 7: (a) Cyclic voltammograms and (b) EIS Nyquist plots of PS/MoO₂ planar asymmetric membrane anode. Inset: equivalent circuit used to fit the plots.

sequence. There is a very sharp cathodic peak at 10 mV for the first scan at 0.1 mV/s, which can be attributed to the decomposition of electrolytes and formation of SEI layer. Two anodic peaks appear at 1.47 and 1.79 V, corresponding to the deintercalation of lithium ions from MoO₂. In the following two scans at 0.1 mV/s, a very broad peak ranging from 1.0 to 1.6 V can be assigned to the intercalation of lithium ions into MoO₂ [6]. When the scan rate is increased from 0.1 to 1.6 mV/s, the overpotentials for lithiation and de-lithiation have been significantly increased as evidenced by the downshifted lithiation potential to ~0.80 V and upshifted de-lithiation potential to above 2.0 V. Although MoO₂ has a metal-like electrical conductivity, the lithium ion diffusivity in MoO₂ is

quite low, $\sim 1 \times 10^{-10} \text{ cm}^2/\text{s}$, thus causing such large overpotentials [46]. This issue could be alleviated by adopting MoO₂ quantum dots with extremely small diffusion lengths [47]. However, ICL might also be elevated since quantum dots have a huge surface area [48]. Correlated lithiation and de-lithiation for MoO₂ and MoO₃ anodes can be expressed by the following reactions (2–4) [24, 46]:

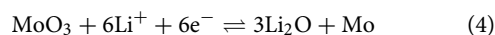
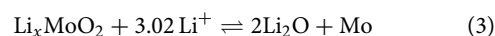


Figure 7b shows the EIS spectra of fully de-lithiated PS/MoO₂ planar asymmetric membrane anode before and after the cycling test, which were fitted using the equivalent circuit as shown in the inset, where R_s , R_{SEI} , and R_{CT} represent ohmic, SEI, and charge transfer resistances, CPE_1 and CPE_2 are constant phase elements related to the SEI layer and electrode surface double layer capacitances, and W_d stands for Warburg diffusion impedance [49]. It can be seen there is no significant change in the ohmic resistance (Table 3), indicating no apparent electrode delamination and detachment occurred during the long-term cycling test. R_{ct} resistance remains nearly constant, implying that lithium ions are fully accessible to the active materials during the cycling test. The large R_{ct} is consistent with the sluggish lithium ion diffusivity in molybdenum oxide as mentioned in the introduction. Slightly decreased SEI resistance is attributed to the gradual formation of stable SEI in the cycling test [50]. The increased CPE values are probably due to the breakup of larger MoO₂ NPs into smaller ones during repeated lithiation and de-lithiation and the formation of tiny Li₂O NPs that are quite capacitive [51, 52]. Since MoO₂ electrode has much higher capacity and larger volume change during lithiation/de-lithiation as compared to commercial graphite anode, it requires multiple cycles to form stable SEI layers, resulting in a significant change of Nyquist plot after the long-term cycling test (Fig. 7b and Table 3). The contact between membrane and current collector has also been slightly deteriorated (5 ohms for the 1st and 8 ohms for the 165th; Table 3), probably due to the slight volume variation of the membrane electrode, which can affect the contact between the copper and membrane. Lastly, the PS/MoO₂ planar asymmetric membrane anode after being cycled for 165 times was retrieved, cleaned using large quantity of diethyl carbonate, and then examined using SEM (S7). The top surface of the electrode remains integral even after being repeatedly lithiated and de-lithiated for 165 times, indicating that the unique

TABLE 3: Extracted equivalent circuit parameters by fitting the Nyquist plots shown in Fig. 7c.

	R_s (ohm)	R_{SEI} (ohm)	R_{CT} (ohm)	CPE_1 ($\mu\text{F}\cdot\text{s}^{(\alpha_1-1)}$)	α_1	CPE_2 ($\mu\text{F}\cdot\text{s}^{(\alpha_2-1)}$)	α_2
1st cycle	5.0	70.6	235	44.1	0.689	624	0.705
165th cycle	8.0	43.2	250	114	0.670	1193	0.709

asymmetric membrane porous structure can efficiently accommodate the large volume changes and stress. Cross-sectional view reveals that the membrane thickness is $\sim 122\ \mu\text{m}$ (S7) after the long-term cycling test as compared to $\sim 119\ \mu\text{m}$ before the cycling test (Fig. 2a). This fact suggests that the electrode didn't experience any significant radial expansion and also explains why the electrode surface remains nearly crack-free after many repeated lithiation and de-lithiation.

Conclusions

It is clearly demonstrated that thermal annealing, geometry, and polymer precursor have significant impacts on the electrochemical properties of nanoporous asymmetric membranes containing MoO_2 and MoO_3 NPs as LIB anode. Planar PS/ MoO_2 asymmetric membrane anode that is carbonized only possesses the most outstanding capacity, cycling stability, and rate performance due to its unique asymmetric porous structure, high electrical conductivity and close contact between the active materials and carbon matrix. After being thermally annealed in air, PS/ MoO_2 membrane is converted to PS/ MoO_3 membrane that has a high initial capacity but poor cyclability. Although the cyclability of fibrous PS/ MoO_2 membrane is comparable to its planar counterpart, the capacity is much lower because the nanoporous surface may hinder the diffusion of lithium ions, especially at high current densities. The type of polymer precursor can also affect the capacity and electrode stability of the membrane electrode. The asymmetric membrane electrode made from PAN has lower capacity and cyclability because planar PAN/ MoO_2 membrane is less nanoporous than planar PS/ MoO_2 membrane, thereby obstructing lithium ion diffusion. Since the membrane porosity can be affected by many factors, including phase inversion temperature, phase inversion time, membrane thickness, concentration of polymer, type of polymers, type of additives, type of solvents and non-solvents, etc., creative modeling and extensive computations are needed to provide necessary guidance in order to dramatically shorten the time input to identify the right experimental parameters to obtain membranes with the most optimal porosity as lithium ion battery anode.

Materials and methods

Fabrication of planar PS/ MoO_2 and PS/ MoO_3 asymmetric membranes

First, ammonium molybdate tetrahydrate $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O})$ was heated at $350\ ^\circ\text{C}$ in air for 12 h to obtain MoO_3 nanoparticles. Next, 2.0 g MoO_3 nanoparticles, 1.0 g polysulfone (PS, $M_n = 60,000$, pellets, Acros), 0.30 g carbon black (CB, TIMCAL SUPER C45 with a surface area of $45\ \text{m}^2\ \text{g}^{-1}$), and 10 mL *N*-methyl-2-pyrrolidone (NMP, Sigma Aldrich, $>99.5\%$) were mixed thoroughly using a planetary ball mill (Acros

International, PQ-N04 Planetary Ball Mill) at 50 rotations per minute (rpm) for 4 h to prepare a uniform slurry. The slurry was then casted into a thin film using a doctor blade with a thickness setting of $200\ \mu\text{m}$. The thin film was immediately immersed into deionized water (DI; $>17\ \text{M}\Omega\cdot\text{cm}$) for 30 min to complete the phase inversion, resulting in the spontaneous formation of asymmetric membrane. As-prepared asymmetric membrane was carbonized at $500\ ^\circ\text{C}$ under the protection of 200 sccm helium gas (99.9999%, Airgas He UHP300) using a Lindberg/Blue M[™] 1100 $^\circ\text{C}$ tube furnace with a ramp rate of $\sim 60\ ^\circ\text{C}\ \text{min}^{-1}$ to produce conductive PS/ MoO_2 planar asymmetric membrane. PS/ MoO_2 planar asymmetric membrane was annealed in air at $380\ ^\circ\text{C}$ for 30 min to obtain PS/ MoO_3 planar asymmetric membrane.

Fabrication of PS/ MoO_2 fibrous asymmetric membrane

A slurry made of 2.0 g MoO_3 nanoparticles, 1.0 g PS, 0.30 g CB, and 10 mL NMP was transferred into a 10 mL syringe (Air-Tite Products Co.) equipped with a 31G needle (Air-Tite Products Co.) and then extruded at a rate of $\sim 1\ \text{mL}\ \text{min}^{-1}$ into DI water to form fibrous asymmetric membrane using a manual arbor press as shown in the supporting information and also methodically described in our previous report [20, 53]. Arbor press was used to create enough compress load to overcome the high viscosity of the slurry. Lastly, the fibrous asymmetric membrane was carbonized at $500\ ^\circ\text{C}$ for 1 h under the protection of 200 sccm helium gas using the Lindberg/Blue M[™] 1100 $^\circ\text{C}$ tube furnace with a ramp rate of $\sim 60\ ^\circ\text{C}\ \text{min}^{-1}$ to obtain conductive PS/ MoO_2 fibrous asymmetric membrane.

Fabrication of PAN/ MoO_3 planar asymmetric membranes

The procedure used to prepare PAN/ MoO_3 planar asymmetric membrane is similar to that for PS/ MoO_3 planar asymmetric membrane except that 1.0 g PS was replaced by 1.0 g polyacrylonitrile (PAN, $M_n \approx 150,000$, powders, Pfaltz & Bauer). Additionally, PAN was carbonized at $800\ ^\circ\text{C}$ since a higher temperature is needed to fully carbonize PAN as reported in the literature [25, 54].

Characterization

Powder X-ray diffractions (PANalytical Empyrean) were scanned from 10 to 90° (two theta) with a step rate of $0.1^\circ/\text{s}$ using Cu K_α radiation ($\lambda = 1.541\ \text{\AA}$), acceleration voltage of 40 kV, and current of 40 mA. A Field Emission Scanning Electron Microscope (JEOL JSM-7600F) attached with a Transmission Electron Detector and an Energy Dispersive X-ray Spectroscopy (EDS) was used for morphological and structural

characterization, elemental mapping, and compositional analyses as well. High-angle annular dark-field (HAADF)-scanning transmission electron microscope (STEM) and energy-dispersive X-ray spectroscopy (EDS) images were collected using a FEI Talos F200X operated at 200 keV at the Center for Functional Nanomaterials at Brookhaven National Laboratory. In addition, using a JEOL 2100 microscope operating at 200 keV, the high-resolution transmission electron microscopy (HRTEM) images were captured. Brunauer–Emmett–Teller (BET) surface areas of asymmetric membranes were measured using a Micromeritics ASAP 2020 Surface Area and Porosimetry Analyzer after the membranes were degassed at 50 μ Torr and 300 $^{\circ}$ C for 30 min. The mass percentage of MoO_3 and MoO_2 in the asymmetric membranes was estimated using a thermogravimetric analyzer (TA Instruments Q50 TGA). High purity compressed air gas (Ultra Zero, Airgas) at a flow rate of 20 mL min^{-1} was employed as the purging gas, and TGA oven temperature was increased from room temperature to 500 $^{\circ}$ C at a rate of 10 $^{\circ}$ C min^{-1} and then held for 30 min. A Thermo Scientific K-alpha + X-ray photoelectron spectroscopy (XPS) system was employed to measure the binding energy of core-level electrons using a monochromatic Al K_{α} X-ray with an energy of 1486.6 eV. The X-ray spot size used for these measurements is 400 μm . While the high-resolution XPS spectra were measured using a pass energy of 50 eV and a dwell time of 50 ms with an energy step size of 0.1 eV, those parameters for measuring the wide-scan survey spectra are 200 eV, 10 ms and 1 eV, respectively.

Electrochemical evaluation of MoO_2 and MoO_3 asymmetric membranes as LIB anode

Electrode was prepared by gluing ~ 2.0 mg asymmetric membrane onto a copper disk (15 mm in diameter and 11 μm thick from MTI Corporation). The glue was made of 0.15 g CB, 0.15 g polyvinylidene fluoride (PVDF, MTI Corporation), and 3 ml NMP. The electrode was then dried at 100 $^{\circ}$ C for at least 4 h to remove moisture and NMP. Lastly, the electrode was assembled into 2032-type coin cell inside an argon-filled glove box using lithium metal (EQ-Lib-LiC25, MTI Corporation) as the counter electrode, polyethylene/polypropylene blend (MTI Corporation) as the membrane separator and 60 μL 1 M LiPF_6 dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) with a volume ratio of 1:1:1 (MTI Corporation) as the electrolyte. The concentration of oxygen and water inside the glove box (LCPW, LC Technology Solutions, INC.) was controlled below 1 ppm. Control electrode was made from 0.60 g MoO_3 NPs, 0.20 g CB, and 0.10 g PVDF dispersed in appropriate amount of NMP, in which the mass percentage of MoO_3 was calculated to be ~ 75 wt% based on the total mass of carbon and MoO_3 , whose value is close to the mass percentage of MoO_3

in PS/ MoO_3 and PAN/ MoO_3 planar asymmetric membranes (Table 1). Galvanostatic cycling tests were conducted using a multi-channel Potentiostat/EIS (BIO-LOGIC VMP3) at room temperature. The cells were charged and discharged at the same current density from 0.01 $\sim$ 3.00 V (vs. Li/Li^+). Two formation cycles were carried out at 30 mA g^{-1} before subsequent cycling and rate tests began. Voltage was scanned between 0.01 and 3.00 V for cyclic voltammetry measurements. A frequency range of 0.1 Hz–1 MHz with 10 mV AC perturbation was employed during electrochemical impedance spectroscopy (EIS) analyses.

Acknowledgments

This work is supported by National Science Foundation Division of Chemical, Bioengineering, Environmental and Transport Systems (NSF CBET Award #1800619). XPS was performed in the Nebraska Nanoscale Facility: National Nanotechnology Coordinated Infrastructure and the Nebraska Center for Materials and Nanoscience (and/or NERCF), which are supported by the National Science Foundation under Award ECCS: 2025298, and the Nebraska Research Initiative. This research also used resources at the Center for Functional Nanomaterials at Brookhaven National Laboratory, which is a U.S. DOE Office of Science Facility under contract DE-SC0012704. J.W. and J. D. also want to acknowledge the generous infrastructural support provided by Georgia Southern University and GSU COUR award.

Author contributions

E.L., L.W., C.J., and X.C. carried out the experiments and participated in scientific discussion and manuscript preparation as well. J.D., O.S., and S.X. performed the experiments. J.W. came up with the research hypothesis, designed the experiments, managed the project, and drafted the manuscript.

Funding

NSF CBET Award #1800619; NSF ECCS Award #2025298; U.S. DOE Office of Science Facility under contract DE-SC0012704.; Georgia Southern University COUR Award.

Availability of data and material

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest All authors declare that they have no conflict of interest.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1557/s43578-021-00347-7>.

References

1. M. Yu, H. Shao, G. Wang, F. Yang, C. Liang, P. Rozier, C.-Z. Wang, X. Lu, P. Simon, X. Feng, Interlayer gap widened α -phase molybdenum trioxide as high-rate anodes for dual-ion-intercalation energy storage devices. *Nat. Commun.* **11**(1), 1348 (2020)
2. W.-J. Li, Z.-W. Fu, Nanostructured WO₃ thin film as a new anode material for lithium-ion batteries. *Appl. Surf. Sci.* **256**(8), 2447 (2010)
3. R. Bekarevich, Y. Pihosh, Y. Tanaka, K. Nishikawa, Y. Matsushita, T. Hiroto, H. Ohata, T. Ohno, T. Minegishi, M. Sugiyama, T. Kitamori, K. Mitsuishi, K. Takada, Conversion reaction in the binder-free anode for fast-charging Li-ion batteries based on WO₃ nanorods. *ACS Appl. Energy Mater.* **3**(7), 6700 (2020)
4. Y. Liu, Y. Jiao, H. Zhou, X. Yu, F. Qu, X. Wu, Rational design of WO(3) nanostructures as the anode materials for lithium-ion batteries with enhanced electrochemical performance. *Nanomicro Lett.* **7**(1), 12 (2015)
5. Y. Wang, Z. Huang, Y. Wang, A new approach to synthesize MoO₂@C for high-rate lithium ion batteries. *J. Mater. Chem. A* **3**(42), 21314 (2015)
6. S. Petnikota, K.W. Teo, L. Chen, A. Sim, S.K. Marka, M.V. Reddy, V.V.S.S. Srikanth, S. Adams, B.V.R. Chowdari, Exfoliated graphene oxide/MoO₂ composites as anode materials in lithium-ion batteries: an insight into intercalation of Li and conversion mechanism of MoO₂. *ACS Appl. Mater. Interfaces* **8**(17), 10884 (2016)
7. S. Fang, D. Bresser, S. Passerini, Transition metal oxide anodes for electrochemical energy storage in lithium- and sodium-ion batteries. *Adv. Energy Mater.* **10**(1), 1902485 (2020)
8. Y. Chen, X. Chen, Y. Zhang, A comprehensive review on metal-oxide nanocomposites for high-performance lithium-ion battery anodes. *Energy Fuels* **35**(8), 6420 (2021)
9. A. Manthiram, A reflection on lithium-ion battery cathode chemistry. *Nat. Commun.* **11**(1), 1550 (2020)
10. L. Zhou, L. Yang, P. Yuan, J. Zou, Y. Wu, C. Yu, α -MoO₃ nanobelts: a high performance cathode material for lithium ion batteries. *J. Phys. Chem. C* **114**(49), 21868 (2010)
11. X. Zhao, W. Jia, X. Wu, Y. Lv, J. Qiu, J. Guo, X. Wang, D. Jia, J. Yan, D. Wu, Ultrafine MoO₃ anchored in coal-based carbon nanofibers as anode for advanced lithium-ion batteries. *Carbon* **156**, 445 (2020)
12. U.K. Sen, S. Mitra, Synthesis of molybdenum oxides and their electrochemical properties against Li. *Energy Procedia* **54**, 740 (2014)
13. M.A. Camacho-López, L. Escobar-Alarcón, M. Picquart, R. Arroyo, G. Córdoba, E. Haro-Poniatowski, Micro-Raman study of the m-MoO₂ to α -MoO₃ transformation induced by cw-laser irradiation. *Opt. Mater.* **33**(3), 480 (2011)
14. R.J. Petersen, Composite reverse osmosis and nanofiltration membranes. *J. Membr. Sci.* **83**(1), 81 (1993)
15. J. Radjenović, M. Petrović, F. Ventura, D. Barceló, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment. *Water Res.* **42**(14), 3601 (2008)
16. B. Nicolaisen, Developments in membrane technology for water treatment. *Desalination* **153**(1), 355 (2003)
17. J. Wu, H. Chen, C. Padgett, Silicon asymmetric membranes for efficient lithium storage: a scalable method. *Energy Technol.* **4**(4), 502 (2016)
18. I. Byrd, H. Chen, T. Webber, J. Li, J. Wu, Self-assembled asymmetric membrane containing micron-size germanium for high capacity lithium ion batteries. *RSC Adv.* **5**(113), 92878 (2015)
19. J. Wu, H. Chen, I. Byrd, S. Lovelace, C. Jin, Fabrication of SnO₂ asymmetric membranes for high performance lithium battery anode. *ACS Appl. Mater. Interfaces* **8**(22), 13946 (2016)
20. M. Li, C. Anderson, P. Beaupre, C. Jin, J. Li, J. Wu, Tin asymmetric membranes for high capacity sodium ion battery anodes. *Mater. Today Commun.* **24**, 100998 (2020)
21. M. Müller, V. Abetz, Nonequilibrium processes in polymer membrane formation: theory and experiment. *Chem. Rev.* (2021). <https://doi.org/10.1021/acs.chemrev.1c00029>
22. G.M. Geise, H.B. Park, A.C. Sagle, B.D. Freeman, J.E. McGrath, Water permeability and water/salt selectivity tradeoff in polymers for desalination. *J. Membr. Sci.* **369**(1), 130 (2011)
23. J. Wienold, R.E. Jentoft, T. Ressler, Structural investigation of the thermal decomposition of ammonium heptamolybdate by in situ XAFS and XRD. *Eur. J. Inorg. Chem.* **2003**(6), 1058 (2003)
24. M. Ihsan, H. Wang, S.R. Majid, J. Yang, S.J. Kennedy, Z. Guo, H.K. Liu, MoO₂/Mo₂C/C spheres as anode materials for lithium ion batteries. *Carbon* **96**, 1200 (2016)
25. J.C. Lee, B.H. Lee, B.G. Kim, M.J. Park, D.Y. Lee, I.H. Kuk, H. Chung, H.S. Kang, H.S. Lee, D.H. Ahn, The effect of carbonization temperature of PAN fiber on the properties of activated carbon fiber composites. *Carbon* **35**(10), 1479 (1997)
26. I. Pinnau, W.J. Koros, Structures and gas separation properties of asymmetric polysulfone membranes made by dry, wet, and dry/wet phase inversion. *J. Appl. Polym. Sci.* **43**(8), 1491 (1991)
27. I.-C. Kim, H.-G. Yun, K.-H. Lee, Preparation of asymmetric polyacrylonitrile membrane with small pore size by phase inversion and post-treatment process. *J. Membr. Sci.* **199**(1), 75 (2002)
28. K.-W. Lee, B.-K. Seo, S.-T. Nam, M.-J. Han, Trade-off between thermodynamic enhancement and kinetic hindrance during phase inversion in the preparation of polysulfone membranes. *Desalination* **159**(3), 289 (2003)
29. C. Barth, M.C. Gonçalves, A.T.N. Pires, J. Roeder, B.A. Wolf, Asymmetric polysulfone and polyethersulfone membranes: effects of thermodynamic conditions during formation on their performance. *J. Membr. Sci.* **169**(2), 287 (2000)

30. J. Zhang, T. Wang, P. Liu, Z. Liao, S. Liu, X. Zhuang, M. Chen, E. Zschech, X. Feng, Efficient hydrogen production on MoNi_4 electrocatalysts with fast water dissociation kinetics. *Nat. Commun.* **8**(1), 15437 (2017)
31. R.K. Sharma, G.B. Reddy, Synthesis and characterization of $\alpha\text{-MoO}_3$ microspheres packed with nanoflakes. *J. Phys. D: Appl. Phys.* **47**(6), 065305 (2014)
32. M. Tang, A.T. Nelson, E.S. Wood, S.A. Maloy, Y.-B. Jiang, Grazing incidence X-ray diffraction and transmission electron microscopy studies on the oxide formation of molybdenum in a water vapor environment. *Scr. Mater.* **120**, 49 (2016)
33. X. Lu, R. Wang, F. Yang, W. Jiao, W. Liu, L. Hao, X. He, Preparation of MoO_3 QDs through combining intercalation and thermal exfoliation. *J. Mater. Chem. C* **4**(28), 6720 (2016)
34. H. Sitepu, B.H. O'Connor, D. Li, Comparative evaluation of the March and generalized spherical harmonic preferred orientation models using X-ray diffraction data for molybdenite and calcite powders. *J. Appl. Crystallogr.* **38**(1), 158 (2005)
35. D.E. Cox, R.J. Cava, D.B. McWhan, D.W. Murphy, A neutron powder diffraction study of the lithium insertion compound LiMoO_2 from 4–440K. *J. Phys. Chem. Solids* **43**(8), 657 (1982)
36. E. Pu, D. Liu, P. Ren, W. Zhou, D. Tang, B. Xiang, Y. Wang, J. Miao, Ultrathin MoO_2 nanosheets with good thermal stability and high conductivity. *AIP Adv.* **7**(2), 025015 (2017)
37. C.F. Holder, R.E. Schaak, Tutorial on powder X-ray diffraction for characterizing nanoscale materials. *ACS Nano* **13**(7), 7359 (2019)
38. D.O. Scanlon, G.W. Watson, D.J. Payne, G.R. Atkinson, R.G. Egdell, D.S.L. Law, Theoretical and experimental study of the electronic structures of MoO_3 and MoO_2 . *J. Phys. Chem. C* **114**(10), 4636 (2010)
39. J. Baltrusaitis, B. Mendoza-Sanchez, V. Fernandez, R. Veenstra, N. Dukstiene, A. Roberts, N. Fairley, Generalized molybdenum oxide surface chemical state XPS determination via informed amorphous sample model. *Appl. Surf. Sci.* **326**, 151 (2015)
40. F. Borgatti, J.A. Berger, D. Céolin, J.S. Zhou, J.J. Kas, M. Guzzo, C.F. McConville, F. Offi, G. Panaccione, A. Regoutz, D.J. Payne, J.-P. Rueff, O. Bierwagen, M.E. White, J.S. Speck, M. Gatti, R.G. Egdell, Revisiting the origin of satellites in core-level photoemission of transparent conducting oxides: the case of n-doped SnO_2 . *Phys. Rev. B* **97**(15), 155102 (2018)
41. L. Fransson, T. Eriksson, K. Edström, T. Gustafsson, J.O. Thomas, Influence of carbon black and binder on Li-ion batteries. *J. Power Sources* **101**(1), 1 (2001)
42. Q. Ai, D. Li, J. Guo, G. Hou, Q. Sun, Q. Sun, X. Xu, W. Zhai, L. Zhang, J. Feng, P. Si, J. Lou, L. Ci, Artificial solid electrolyte interphase coating to reduce lithium trapping in silicon anode for high performance lithium-ion batteries. *Adv. Mater. Interfaces* **6**(21), 1901187 (2019)
43. I. Byrd, J. Wu, Asymmetric membranes containing micron-size silicon for high performance lithium ion battery anode. *Electrochim. Acta* **213**, 46 (2016)
44. K. Goldshtein, K. Freedman, D. Schneier, L. Burstein, V. Ezersky, E. Peled, D. Golodnitsky, Advanced multiphase silicon-based anodes for high-energy-density Li-ion batteries. *J. Electrochem. Soc.* **162**(6), A1072 (2015)
45. Q.-L. Wu, S.-X. Zhao, L. Yu, L.-Q. Yu, X.-X. Zheng, G. Wei, In situ synthesis and electrochemical performance of MoO_{3-x} nanobelts as anode materials for lithium-ion batteries. *Dalton Trans.* **48**(34), 12832 (2019)
46. S. Yoon, K.-N. Jung, C.S. Jin, K.-H. Shin, Synthesis of nitrated MoO_2 and its application as anode materials for lithium-ion batteries. *J. Alloys Compd.* **536**, 179 (2012)
47. L. Zhong, J. Guo, L. Mangolini, A stable silicon anode based on the uniform dispersion of quantum dots in a polymer matrix. *J. Power Sources* **273**, 638 (2015)
48. P. Wu, S. Chen, A. Liu, The influence of contact engineering on silicon-based anode for Li-ion batteries. *Nano Select* **2**(3), 468 (2021)
49. A.R.C. Bredar, A.L. Chown, A.R. Burton, B.H. Farnum, Electrochemical impedance spectroscopy of metal oxide electrodes for energy applications. *ACS Appl. Energy Mater.* **3**(1), 66 (2020)
50. C. Li, C. Liu, W. Wang, J. Bell, Z. Mutlu, K. Ahmed, R. Ye, M. Ozkan, C.S. Ozkan, Towards flexible binderless anodes: silicon/carbon fabrics via double-nozzle electrospinning. *Chem. Commun.* **52**(76), 11398 (2016)
51. H.-S. Kim, J.B. Cook, S.H. Tolbert, B. Dunn, The development of pseudocapacitive properties in nanosized- MoO_2 . *J. Electrochem. Soc.* **162**(5), A5083 (2015)
52. S. Lörger, K. Narita, R. Usiskin, J. Maier, Enhanced ion transport in Li_2O and Li_2S films. *Chem. Commun.* **57**(53), 6503 (2021)
53. J. Wu, C. Anderson, P. Beaupre, S. Xu, C. Jin, A. Sharma, Co-axial fibrous silicon asymmetric membranes for high-capacity lithium-ion battery anode. *J. Appl. Electrochem.* **49**(10), 1013 (2019)
54. M. Jing, C.-G. Wang, Q. Wang, Y.-J. Bai, B. Zhu, Chemical structure evolution and mechanism during pre-carbonization of PAN-based stabilized fiber in the temperature range of 350–600°C. *Polym. Degrad. Stab.* **92**(9), 1737 (2007)